MONOTERPENE EMISSIONS FROM PINE TREES AND THEIR CONTRIBUTIONS TO AMBIENT AIR QUALITY IN A SOUTHEASTERN PINE FOREST

By

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This work is dedicated to my family, especially my beloved wife Mi-kyung and my son Yoo-hwan.

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TABLE OF CONTENTS

ACKNOWLEDGMENTS iii

LIST OF TABLES vii

LIST OF FIGURES xii

ABSTRACT xvi

CHAPTERS

1 INTRODUCTION 1

Rationale. 1
Research Objectives. 4

2 BACKGROUND 6

General Description 6
Review of Literature 8
Sampling Techniques for Pine Tree Emissions . . 8
Vegetation Enclosure Techniques 8
Micrometeorological Techniques 21
Atmospheric Tracer Techniques 26
Multi-Port Sampling Device (MSPD) Approach 31
Environmental Gas Exchange Chamber . . . 31
Sampling Approaches in Characterizing and
Estimating Airborne Monoterpenes 36
Choice of Sorbents 41
Hydrocarbon Analysis and Calibration Techniques 48
Hydrocarbon Analysis Approaches 48
Calibration Techniques 50
Air Quality Measurements 51

3 RESEARCH METHODOLOGY 57

Experimental Methods 57
General Description of Field Site and Laboratory Systems 57
Development of Analytical Methods. 62
Identification of Compounds 73
Development of GC Calibration Procedures . 77
Development of a Sampling Technique for Estimating Monoterpene Emissions from Vegetation (Trees) . 88
Approach to Sampling for Estimating Airborne Monoterpenes 102

4 RESULTS AND DISCUSSION 107

General Description 107
Terpene Emission Measurements 111
Seasonal Trends in Biogenic Hydrocarbon Emission Rates 112
Slash Pine Emissions 113
Loblolly Pine Emissions 135
Seasonal Effects on Terpene Emission Rates . 151
Temperature Effects on Pine Emissions. . . . 158
Reproducibility Tests for Biogenic Source Enclosure System 164
Rough Handling Effects on Pine Emissions . . 168
Needle Surface Wetness Effects on Pine Tree Emissions 172
Needle Surface Wetness Effects on Slash Emissions 173
Needle Wetness Effect on Loblolly Pine Emissions 178
Emission Rate Comparison 182
Ambient Air Measurements 184
Seasonal Trends in Monoterpene Concentrations 185
Second Quarter (Spring) of 1994 185
Third Quarter (Summer) of 1994 191
Fourth Quarter (Fall) of 1994 199
First Quarter (Winter) of 1995 204
Second Quarter (Spring) of 1995 207
Relationship Between Ambient Monoterpene and Ozone Concentrations 213

Second Quarter (Spring) of 1994. 214
Third Quarter (Summer) of 1994 216
Fourth Quarter (Fall) of 1994 217
First Quarter (Winter) of 1995 218
Relationship between Ambient Air Temperatures and Monoterpene Concentrations 218
The Relationship between Emission Sources and Sinks 219
Effects of Age on Slash and Loblolly Pine Emissions 224
Long Term Variations in Pine Tree Emission Rates and Ambient Terpene Concentrations 226

5 CONCLUSIONS 232

Development of Analytical and Sampling Approaches 232
Emission Rate Measurements 233
Ambient Air Measurements 235

6 RECOMMENDATIONS 238

REFERENCES 242

BIOGRAPHICAL SKETCH 252

LIST OF TABLES

Table page

2-1. Tenax versus Canister Collection Data 40

2-2. Desorption of Terpene Hydrocarbons at 300°C 44

3-1. GC Configurations and Operating Conditions 65

3-2. EPA Default and Optimal Recommended Operating Conditions for Transfer of Biogenic Hydrocarbons to GC Systems using Tekmar 5010 Thermal Desorption Systems 68

3-4. Comparison of Mass/Charge Ratios for α-pinene between a Standard and a Field Sample using Perkin Elmer 8420 GC/ITD 81

3-5. Comparison of differences in results from two calibration methods for major terpene hydrocarbons . 89

3-6. Testing of a Modified Vegetation Enclosure Technique.96

4-1. Statistical Analysis of Terpene Emission Rates (TERs) from Slash Pine Saplings during the 3rd Quarter (Summer) of 1994 115

4-2. Statistical Analysis of Terpene Emission Rates (TERs) from Slash Pine Saplings during the 4th Quarter (Fall) of 1994 116

4-3. Statistical Analysis of Fractional TERs for Slash Pine during the 3rd Quarter of 1994 121

4-4. Statistical Analysis of Fractional TERs for Slash Pine during the 4th Quarter of 1994 122

4-5. Statistical Analysis of Terpene Emission Rates (TERs) from slash pine saplings during the 1st Quarter of 1995 125

4-6. Statistical Analysis of Terpene Emission Rates (TERs) from slash pine saplings during the 2nd Quarter of 1995 126

4-7. Terpene Emission Rates from a Slash Pine Branch with an elongating Bud 130

4-8. Fractional HC Contribution to Total Emission Rates from Slash Pine with an elongating Bud 130

4-9. Statistical Analysis of Fractional TERs for Slash pine saplings during the 1st Quarter of 1995. 133

4-10. Statistical Analysis of Fractional HC Contributions to Total TERs for Slash Pine Saplings during the 2nd Quarter of 1995. 134

4-11. Statistical Analysis of Terpene Emission Rates (TERs) from Loblolly Pine saplings during the 3rd Quarter of 1994 138

4-12. Statistical Analysis of Terpene Emission Rates (TERs) from Loblolly Pine saplings during the 4th Quarter of 1994 138

4-13. Statistical Analysis of Fractional HC Contributions to TERs for Loblolly Pine during the 3rd Quarter of 1994 141

4-14. Statistical Analysis of Fractional HC Contributions to TERs for Loblolly Pine during the 4th Quarter of 1994 141

4-15. Statistical Analysis of Terpene Emission Rates (TERs) from Loblolly Pine saplings during the first Quarter of 1995 147

4-16. Statistical Analysis of Terpene Emission rates (TERs) from Loblolly Pine Saplings during the 2nd Quarter of 1995. 148

4-17. Boiling Points and Vapor Pressures of Monoterpenes 152

4-18. Statistical Analysis of Fractional Hydrocarbon Contributions to TERs for Loblolly Pine Saplings during the 1st quarter of 1995 153

4-19. Statistical Analysis of Fractional Hydrocarbon Contributions to TERs for Loblolly Pine Saplings during the 2nd Quarter of 1995 154

4-20. Reproducibility of Slash Pine Emission Measurements 167

4-21. Reproducibility of Loblolly Pine Emissions Measurements 168

4-22. Comparison between Environmental and Enclosure Bag Temperature (T) 174

4-23. Needle Wetness Study #1 of Slash Pine Terpene Emission Rates ($\mu g/m^2$-hr) 175

4-24. Comparison of Consecutive Daily Samples of Slash Pine Emission rates($\mu g/m^2$-hr) 177

4-25. Needle Wetness Study #2 of Slash Pine Terpene Emission Rates ($\mu g/m^2$-hr) 177

4-26. Needle Wetness Study #1 of Loblolly Pine Terpene Emission Rates($\mu g/m^2$-hr) 179

4-27. Needle Wetness study #2 of Loblolly Pine Terpene Emission Rates($\mu g/m^2$-hr) 181

4-28. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 2nd Quarter (Spring) of 1994 . . 188

4-29. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 2nd Quarter (Spring) of 1994 188

4-30. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 3rd Quarter (Summer) of 1994 . . 194

4-31. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 3rd Quarter (Summer) of 1994 198

4-32. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 4th Quarter (Fall) of 1994 . . . 201

4-33. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 4th Quarter (Fall) of 1994 201

4-34. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 1st Quarter (Winter) of 1995 . . 206

4-35. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 1st quarter (Winter) of 1995 206

4-36. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 2nd Quarter (Spring) of 1995 . . 211

4-37. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 2nd Quarter (Spring) of 1995 211

4-38. The Relationship between the Fractional Hydrocarbon Emission Rates for Slash Pine and Fractional Ambient Hydrocarbon Composition 222

4-39. Comparison of β/α Ratios for Slash Pine Emission and Ambient Air Samples 222

4-40. Comparison of the Fractional Hydrocarbon Compositions and the β/α Ratios between 4 & 7 yr old Slash Pines. 225

4-41. Monthly and Annual Averages of Total Terpene Emission Rates from Slash and Loblolly Pine Trees 227

4-42. Quarterly Average of Total Terpene Emission Rates from Slash and Loblolly Pine Trees 228

LIST OF FIGURES

Figure Page

2-1. Vegetation Emission Sample Collection System 14

2-2. Apparatus for Direct Measurement of Rates of Emission of Natural Hydrocarbons 20

2-3. Meteorological Sensor and Hydrocarbon Sampling Locations used in the Washington Douglas Fir Forest . . . 23

2-4. Forest Sampling System and Loblolly Pine Forest Vertical Gradients 25

2-5. Area of Study 30

2-6. Plant Gas-Exchange Chamber 32

2-7. Seasonal Variations in Diurnal Ozone Concentrations at Cary Forest FL in 1988-89 53

2-8. Ozone Daily Averages and Maximums for Cary Forest, FL in 1989 54

3-1. Flow Diagram for Continuous Air Quality Monitoring at Cary Forest Field Site 59

3-2. Layout of Cary Forest Site Showing Ambient and Vegetation Enclosure Technique (VET) Sampling Locations . 61

3-3. Analytical Systems Configurations for Qualification and Quantification of Hydrocarbons 64

3-4. Design of a Reproducible, Versatile, & Multiple Sample Containment, Transfer & GC Introduction System . . . 71

3-5(a). Typical Gas Chromatogram for a Standard Mixture of Terpene Compounds and P-xylene Internal Standard for the GC/ITD/Tekmar System 75

3-5(b). Typical Gas Chromatogram for a Standard Mixture of Terpene Compounds and P-xylene Internal Standard for the GC/FID/Tekmar System 76

3-6(a). Mass Spectral Cracking Pattern for α-pinene from a Field Sample using Perkin Elmer 8500GC/ITD/Tekmar System 79

3-6(b). Mass Spectral Cracking Pattern for α-pinene from a Field Sample using Perkin Elmer 8500GC/FID/Tekmar System 80

3-7. Typical Calibration Curve for α-pinene using Perkin Elmer 8500GC/FID and Tekmar 5010 GT System 84

3-8. Apparatus for Dynamic Dilution System 86

3-9. Approach to Equilibrium and Flush Test Using Ethanol Injection into Zero Air & 19L Tedlar Bag 93

3-10. Sampling Train for Developed Emission Rate Determinations 94

3-11. Sampling Train Used for Collecting Hydrocarbons in Ambient Air at the Cary Forest Site. 104

4-1. Accuracy Control Chart for Monoterpenes & P-Xylene 109

4-2. Precision Control Chart for Syringe Injected alpha-Pinene 110

4-3. Terpene Emission Rate Trends for Slash Pine during the 3rd and 4th Quarters of 1994 114

4-4. Fractional distributions of HC Emission Rates for Slash Pine during the 3rd and 4th Quarters of 1994 . . . 119

4-5. Terpene emission rate trends for Slash Pine Saplings during the 1st and 2nd Quarters of 1995 124

4-6. Fractional HC Distributions of Emission Rates for Slash Pine Saplings during the 1st and 2nd Quarters of 1995 . 131

4-7. Terpene Emission Rate Trends for Loblolly Pine Saplings during the 3rd and 4th Quarters of 1994 137

4-8. Distributions of Fractional HC Emission Rates for Loblolly Pine Saplings during the 3rd and 4th Quarters of 1994 140

4-9. Terpene Emission Rate Trends for Loblolly Pine Saplings during the 1st and 2nd Quarters of 1995 146

4-10. Fractional HC Composition to Total Emission Rates for Loblolly Pine Saplings during the 1st and 2nd Quarters of 1994 150

4-11. Variations in Total and Fractional HC Contributions in Slash Pine Emission Samples at Environmental Temperatures in the Range from 25.8 °C to 32.1 °C 155

4-12. Variations in Total and Fractional HC Contributions in Loblolly Pine Emission Samples at Environmental Temperatures in the Range from 29.5 °C to 32.1 °C 156

4-13. Dependence of Loblolly Pine Emission Rates on Environmental Temperature 160

4-14. Dependence of Slash Pine Emission Rates on Environmental Temperature for September through December, 1994 162

4-15. Dependence of Slash Pine Emission Rates on Environmental Temperature in February of 1995 . . 163

4-16. Dependence of Slash Pine Emission Rates on Environmental Temperature during March and April of 1995 165

4-17. Seasonal Ambient Terpene Concentration Trends during the 2nd Quarter of 1994 186

4-18. Fractional Distribution of Ambient Hydrocarbon Observed during the 2nd Quarter of 1994 190

4-19. Seasonal Ambient Terpene Concentration Trends during the 3rd Quarter of 1994 192

4-20. Fractional Distribution of Ambient Hydrocarbon Observed during the 3rd Quarter of 1994 197

4-21. Seasonal Ambient Terpene Concentration Trends during the 4th Quarter of 1994 202

4-22. Fractional Distribution of Ambient Hydrocarbon Observed during the 4th Quarter of 1994 203

4-23. Ambient Terpene Concentration Trends during the 1st Quarter of 1995 205

4-24. Fractional Distributions of Ambient Hydrocarbon Observed during the 1st Quarter of 1995 208

4-25. Seasonal Ambient Terpene Concentration Trends during the 2nd Quarter of 1995 209

4-26. Fractional Distributions of Ambient HC Concentration Variations during the 2nd Quarter of 1995 212

4-27. Observed Total Monoterpenes Ambient Concentrations vs Concentrations during the 2nd Quarter,1994 . . . 215

4-28. Influence of Temperature on Ambient Monoterpene Levels during the 2nd Quarter, 1994 220

4-29. Variation of Total Monoterpene Emission Rates from Slash pine Saplings from 7/8/94 to 6/14/95 . . . 229

4-30. Variation of Total Monoterpene Emission Rates from Loblolly pine Saplings from 7/27/94 to 6/14/95 . 230

4-31. Variation of Total Monoterpene Concentrations in Ambient Air from 4/11/94 to 6/14/95 231

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By

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Major Department: Environmental Engineering Sciences

A field study, sponsored by the National Institute for Global Environmental Change (NIGEC), has been conducted to estimate emission factors of biogenic hydrocarbons from southern pines. In addition, the influences of specific climate variables on these emission factors have been investigated. Sampling, calibration, and analysis techniques have been developed and tested for determination of monoterpene emission rates in a north central Florida pine forest. A portable vegetation enclosure chamber was designed and constructed of Tedlar. Following laboratory testing for

CHAPTER 1
INTRODUCTION

Rationale

In recent years there has been increased interest in the potential environmental effects of global climate change. Of specific interest is the role that climate change may play in altering biogenic non-methane hydrocarbon (NMHC) emissions from trees and the subsequent impact of this perturbation on air quality and ozone formation. Measurements of natural NMHC emissions in the 1960s have suggested that global and continental scale emissions of natural sources overshadow those from anthropogenic sources (Rasmussen, 1972; Dimitriades, 1981). In addition, the potential effects of biogenic NMHC emissions on ozone formation has attracted attention due to the possible influence of ozone on the production of acid deposition species. Since the atmospheric chemistry of sulfur dioxide, nitrogen oxides, and reactive NMHCs are coupled in a complex way, natural hydrocarbon

emissions have become an important input requirement for both regional acid deposition and photochemical oxidant models (Novak and Reagan, 1986).

Trees are the principal emitters of natural non-methane hydrocarbons in the United States, where the principal chemical species emitted are α-pinene and isoprene (Altshuller, 1983). On a nationwide basis, biogenic sources are estimated to produce from 30 to 60 Teragrams (Tg) of carbon (C) per year, whereas anthropogenic hydrocarbon sources account for only about 18 Tg of C per year (Altshuller, 1983; Lamb et al., 1987). Winer et al., (1983) estimated that natural hydrocarbon (NHC) emissions exceed anthropogenic hydrocarbon (AHC) emissions by factors from about 4 to 10.

In the southeastern United States, the rural and urban landscapes are dominated by forests (about 50 percent of all land is forested) (U.S.D.A. Forest Service, 1988). Approximately half of the southern forests consist of pine species, especially loblolly (*Pinus taeda* L.) and slash (*Pinus elliottii* Engelm.) pines, which are the most important timber producing species that are commercially grown in this region of the U.S. (Johnson and Allen, 1994). Both species of pine trees have been shown to be substantial emitters of

monoterpenes (Tingey, 1981; Arnts et al., 1982); however, many of the early studies of monoterpene emissions could be biased because investigators relied on the use of controlled environments and studied very small (less than 25 cm in height) and/or very young (less than 15 months old) trees. There is still a need to measure and compare the rates of monoterpenes emitted from saplings of these two important pine species with the same age, in the field and during the same period or season, in order to understand and identify those environmental factors that control the nature and relative contributions of these species to ambient monoterpene levels.

Emphasis has been placed on how to model individual key natural NMHCs, such as α-pinene and isoprene, in chemical mechanisms for air quality simulations (Novak and Reagan, 1986). The accuracies of estimates for both natural and anthropogenic emission inventories, however, that are used in these models may be suspect. This problem, in large part, stems from apparently contradictory measurements of these compounds in ambient air and the further possibility of measurement design errors biasing emissions data. In order to generate reliable estimates of emissions for specific biogenic NMHCs in the southeastern region, more detailed representative

and accurate measurements of seasonal natural NMHC emissions are required. A review of the difficulties encountered by previous workers in obtaining representative and reproducible biogenic emissions data suggested that the development of a new sampling and analysis approach was needed. The following objectives were developed to determine the direction and scope of the research project.

Research Objectives

In order to achieve the principal objectives, it was essential to accomplish the following two fundamental objectives.

1. To develop, test, and validate a sampling technique for measuring emission rates of monoterpenes from slash and loblolly pines under a variety of natural atmospheric conditions.
2. To develop analytical and calibration techniques for accurate and precise measurements of monoterpenes in air.

The principal objectives of this overall project are as follows:

1. To investigate environmental factors controlling emission rates of monoterpenes from slash and loblolly pine trees in a north central Florida forest.
2. To determine and compare emission rates and fractional compositions of terpenes from the two species of pine saplings of interest.
3. To investigate seasonal variations in terpene emission rates and corresponding terpene concentrations in ambient air at the site.
4. To study the relationships between terpene emission rates and ambient air terpene concentration levels.
5. To investigate possible relationships between local concentrations of ozone and monoterpene in ambient air at a forested site in the southeastern U.S.

CHAPTER 2
BACKGROUND

General Description

The importance of plant-emitted hydrocarbons in atmospheric chemistry was first emphasized by Went in the 1950s (Went, 1960). It was suggested that aerosol particles produced by oxidation of biogenic hydrocarbons could be the cause of the blue haze often observed over heavily forested areas, such as the Great Smoky Mountains (Went, 1960). Because volatile organic compounds (VOCs) such as natural non-methane hydrocarbon (NMHC) emissions are critical in controlling hydroxyl radical (OH) concentrations in the troposphere, they may also play an important role in determining the growth rate of atmospheric methane (CH_4) and carbon monoxide (CO) concentrations. Infrared absorbing compounds such as methane influence the radiative balance of the atmosphere, which in turn is related to global temperature and precipitation patterns, thus, there is a clear link

between natural VOC emissions and global climate (Guenther et al., 1994).

The effect of natural NMHC emissions on ozone formation has been a topic of interest for several decades and has recently received renewed attention because of the potential influence of ozone on the production of acid deposition and photochemical species. Natural hydrocarbon emissions have become a critical input requirement for regional acid deposition and oxidant models (Novak and Reagan, 1986). Evaluation of the important roles that plant-emitted hydrocarbons play in atmospheric chemistry requires that accurate measurement of biogenic hydrocarbon emission rates and their ambient concentrations be conducted to ascertain their specific contributions to the overall VOC burden of a regional airshed.

It is necessary, therefore, to review and assess procedures employed in the sampling and analysis of plant-emitted hydrocarbons. Related meteorological and air quality measurements, such as those for ambient air temperatures and ozone concentrations, etc., will be discussed later.

Review of Literature

Sampling Techniques for Pine Tree Emissions

There are three types of field methods and one laboratory method which have been recently used to measure HC emission rates from trees. The field methods include vegetation enclosure (VET), micrometeorological (MM), and atmospheric tracer (AT) techniques. The laboratory approach involves a gas exchange chamber (GEC). Problems encountered by investigators employing these techniques suggest that there is a need for the development and application of more advanced sampling and analytical techniques, which address the problems encountered in previous work.

Vegetation Enclosure Techniques

The VET method involves placing an enclosure chamber around selected vegetation in order to isolate it from some of the variables encountered in the surrounding environment (Zimmerman, 1979a).

The advantages of this technique are as follows:

1. Higher concentrations of emissions can usually be attained, which allows for using simpler analytical techniques.

2. No model is required to determine source strengths because source emissions are directly measured.

3. Better control over environmental variables (temperature, relative humidity, light and wind speed) can be attained that might affect emission rates. If these variables are controlled or better understood it is easier to more accurately spatially and temporally extrapolate hydrocarbon emission rates .

4. Sample site selection, when using vegetative enclosure techniques, is not as critical as is the case for micrometeorological or atmospheric tracer techniques. Usually this approach allows for emissions testing even in those areas experiencing high anthropogenic hydrocarbon concentrations.

5. As a result of the advantages described above, sampling programs tend to be less expensive and more portable than those for the other techniques.

There are a number of different types of vegetation enclosure methods (Zimmerman, 1979a) that have been used. Each of these approaches has different characteristics. as described below.

Static Chambers. The static chamber approach has been used by Rasmussen (1972) in field studies of plant emissions.

In this method, a portion of vegetation is enclosed for a specific period of time and a sample is collected from the chamber at the completion of a hydrocarbon accumulation time.

Disadvantages of this method include the following:

1. If the enclosure is rigid, anthropogenic (or ambient) VOCs can invade the chamber as the sample is withdrawn.

2. Also, the chamber is filled with ambient air initially when the whole or a portion of the vegetation is enclosed. If ambient anthropogenic VOC concentrations are high they may obscure the vegetation emissions.

Regulated Enclosures. This more sophisticated type of enclosure has often been used by forest researchers to evaluate seasonal fluctuations of CO_2 emissions from specific portions of a branch. The regulated chamber technique provides for control of temperature, relative humidity, and frequently even solar radiation. These enclosures are designed to maintain long-term environmental equilibrium and environmental control over that portion of the vegetation of interest or the whole plant. Disadvantages of this sampling technique are as follows:

1. The most common materials of construction include Plexiglass, neoprene gaskets, and other plastic components which may emit VOCs.

2. Long-term equilibrium invariably requires the circulation of air through a conditioning system which cools and controls the humidity of the environment. VOC emissions could conceivably be removed, modified, or degraded in such a system.

3. Regulated enclosures are usually designed to be semi-permanent, therefore, a wide variety of species can not be sampled as would be required in an emission inventory program (Zimmerman, 1979a).

Compensated Chambers. Compensated chambers are a class of enclosure which attempt to compensate for the intrinsic enclosure effects of temperature and moisture build-up. This type of chamber is often quite large and can enclose a whole tree. The technique relies upon a fast exchange rate (up to eight exchanges per minute) of the air inside the chamber to minimize the buildup of heat and metabolic by-products. Usually the chamber has a filter at the inlet and a collecting device at the outlet. Often, the tops of the chambers are painted white to minimize radiative heating. However, the

temperatures within these chambers may exceed temperatures of 44°C (6°C above ambient air temperature) even when an air exchange rate of 3.5 times per minute is used (Zimmerman, 1979a).

The disadvantages of using a compensated chamber are as follows:

1. The high flow rates required result in low sample concentrations that necessitate a high degree of analytical sensitivity.

2. Air filtering and sample collection techniques required by this method would be quite complicated, particularly if it was necessary to quantify the full range of organic emissions.

3. Compensated chambers typically are semi-portable at best and are usually designed for long-term installation.

4. The cost of using compensated chambers would be very high for a widespread, short-term sampling and analysis project.

Semi-Static Enclosures. After evaluating the advantages and disadvantages of the preceding techniques and performing a preliminary collection of samples using a static system, a combined static/dynamic sampling procedure was identified and has evolved for use in the current project. The equipment and

procedures involved in collecting vegetative emission samples are illustrated in Figure 2-1.

Basically, this methodology has evolved from the preceding technologies and involves enclosing a portion of vegetation (branch) with a Teflon bag, removing the ambient air inside the bag, causing the bag to collapse around the branch, and collecting a sample of air from the collapsed bag (see Figure 2-1). The bag is then quickly filled with a known volume of zero-air, which is VOC free, and has a controlled level of CO_2. After the bag is partially inflated, another sample is collected while zero-air continues to flow into the enclosure at a rate slightly higher than the sampling flow rate. The difference between the hydrocarbon contents of the collapsed and zero-air filled bags divided by the time interval between the two samples, yields the emission rate of the hydrocarbons from the vegetation. This hydrocarbon emission rate can then be divided by a foliage unit such as biomass (or surface area) to provide an emission rate per unit vegetation mass per unit time. Total enclosure time is of the order 15 minutes.

The semi-static enclosure method has several advantages over other vegetation enclosure approaches:

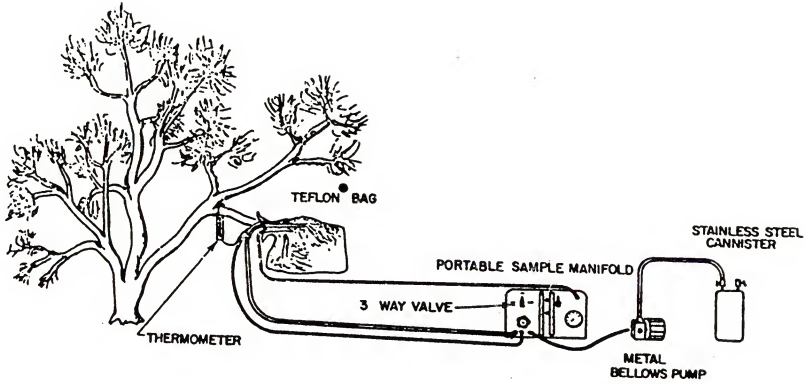


Figure 2-1. Vegetation Emission Sample Collection System.

Source: Zimmerman, 1979a

1. The short enclosure time and the large volume of zero-air used minimizes heat build-up and water vapor accumulation, which ensures that the emission rates are not disturbed.

2. The ultraclean air entering the enclosure and the organic emissions which accumulate in the zero-air enhance analytical sensitivity and precision.

3. The equipment is fully portable. A wide variety of vegetation emission samples can be collected in a relatively short period of time in the field.

4. Emission samples can be collected practically anywhere, the procedure is not site-selective since anthropogenic contributions to ambient air are minimized.

The disadvantages of this static/dynamic sampling approach are as follows:

1. A portable source of clean zero-air may not be readily available.

2. Each major vegetation type must be sampled (a drawback common among enclosure techniques).

3. Possible disturbance of the vegetation emissions may result from the sample collection procedure. This disadvantage is also common among those methodologies which do not remain "outside the system" (Zimmerman, 1979a).

Lamb et al.(1984) applied the semi-static enclosure method in studies of natural HC emission rates. Vegetation enclosure samples in each of the study areas were obtained using a branch enclosure method. This technique involved enclosing a branch in a 100 L Tedlar bag, collecting a background sample from the bag, filling the bag with hydrocarbon-free air, and collecting a second sample of the bag air after a measured length of time. When these measurements of emission rates are used to develop an area emission inventory, the individual branch emission rates (μg/gdw-hr) were multiplied by a specific biomass factor (gdw/m^2) to give the land area emission flux (μg/m^2-hr) (Lamb et al., 1984). However, this emission flux calculation includes uncertainties resulting from variability in biomass densities (estimated error = ± 25%) and errors in the distribution of land use (estimated error = ± 15%) (Lamb et al., 1987). Zimmerman (1979b) estimated that the pine biomass factor for the pine plantation canopies in the Tampa/St.Petersburg area in Florida was about 650 gdw/m^2.

Modified Semi-Static Enclosure with Tracer Test. The equipment and set-up used to collect branch enclosure samples from vegetation are very similar to that shown in Figure 2-1.

Glass thermometers were used to monitor temperatures inside and outside the enclosure. In the standard procedure, the thermometer was placed out of direct sunlight along the branch, and two lengths of Teflon tubing were also situated along the branch. The following sequence of events indicated below was followed:

1. The Teflon bag was carefully placed over the branch and sealed by wrapping with Velcro. Immediately after enclosure of the branch, a background sample was pumped into a 6 liter electropolished stainless steel canister via a battery-operated metal bellows pump.

2. Hydrocarbon-free air was flushed into the bag, and after the bag was inflated, a known volume and known quantity of sulfur hexafluoride (SF_6) was injected into the bag in order to determine the enclosure volume. Air was continuously recirculated through the bag, and after a measured period of time (~6 min) an emission sample was withdrawn from the bag into another evacuated canister.

3. The bag was removed and the branch clipped and dried to determine the weight of the enclosed leaves.

The emission rate (E) is given in terms of micrograms HC per gram dry leaf biomass per hour, and the corresponding

emission flux (F) is given in terms of micrograms HC per square meter per hour.

$$E = \{ C_2 \cdot (V_1 + V_2) - C_1 \cdot V_1 \}/(T \cdot M) \quad (1)$$

$$F = E \cdot B \quad (2)$$

where : C_1 = HC background concentration, C_2 = HC emission sample concentration, T = time between collection of the background and emission samples, V_1 = initial volume of the enclosure, V_2 = volume of zero-air added to the enclosure, M = dry weight of the leaves or needles on the branch, B = biomass factor appropriate for the particular forest site (Lamb et al., 1985).

More recently, Khalil and Rasmussen (1992) applied this modified semi-static enclosure method in his forest hydrocarbon measurement study. The samples (three samples were collected in each experiment--two from a branch and one from background air) of emissions from branches were collected in Tedlar bags. The bags had previously been tested and were shown not to produce hydrocarbons. The samples were brought to the laboratory and analyzed from 1 to 3 days after collection. Measurements of hydrocarbon samples were carried out with a GC with FID according to EPA's Standard Method TO14 (Khalil and Rasmussen, 1992).

Plant Enclosure with Dynamic Flow. The original plant enclosure methods using dynamic flow systems were designed for emission measurements from fruit and nut trees and large agricultural crop plants (e.g., tomato) (Winer et al., 1989). The enclosure chambers were constructed from 2 mil Teflon film suspended from an external PVC frame measuring approximately 0.5 m x 0.5 m x 1 m (~150 L volume)(see Figure 2-2). The chamber was equipped with a stirring motor with a Teflon-coated blade, and inlet and outlet ports suitable for introduction of matrix air and withdrawal of analytical samples. Medical breathing air (Liquid Air; 99.6% stated purity level) was mixed with carbon dioxide (360 ppmv; ambient level) before entering the plant enclosure chamber. The inlet humidity was preset whereas a humidity indicator was used for monitoring the humidity in the chamber. The dynamic flow chamber can be considered a completely mixed flow reactor. The plant emission samples should be taken only after steady state equilibrium has been achieved. A flush time of 10 minutes at a flow rate of ~45 L/min was used before sampling hydrocarbon emissions in the chamber (Winer et al., 1989).

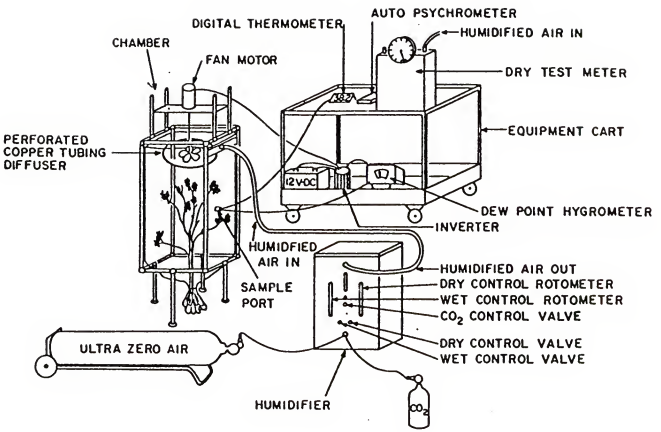


Figure 2-2. Apparatus for Direct Measurement of Rates of Emission of Natural Hydrocarbons.
Source: Winer et al., 1983

Micrometeorological Techniques

Micrometeorological approaches to estimating plant emissions are based upon micrometeorological surface layer theory. The methods involve measurement of HC concentration gradients above an essentially infinite, uniform plane source. Temperature, wind speed, and water vapor concentration gradients must also be measured. The meteorological data are used to determine the eddy diffusivity so that the hydrocarbon flux can be calculated from the concentration gradient. These methods have primarily been used as independent checks upon enclosure-type measurements. Micrometeorological techniques are difficult to setup, and have extremely stringent sensor and site operation requirements (Lamb et al, 1987).

Aerodynamic Gradient Profile Method. In the gradient profile approach, the flux of a particular hydrocarbon is determined from measurements of vertical eddy diffusivities (K_z) and vertical HC concentration profiles (dC/dz) collected vertically along a tower rising above the forest canopy. HC fluxes are calculated from surface layer theory, where the flux is given as follows:

$$F = - K_z \cdot (dC/dz) \qquad (3)$$

Vertical diffusivity, K_z, is obtained from vertical wind speed

and temperature profiles (Dyer, 1974; Benoit, 1977). Meteorological sensors and HC samplers were positioned on the tower at several levels rising above the canopy. The experimental system used at the Washington study site shown in Figure 2-3 indicates the number and types of sensors employed in these studies. During each gradient profile experiment at the hardwood forest, 30 minute-average air samples were collected at six levels on the tower using Teflon sampling pumps and 6-L Tedlar bags (Lamb et al, 1984). For experiments at a coniferous forest, 30 minute-average air samples were collected at five levels on the tower in stainless steel tubes packed with 0.5-g Tenax-GC adsorbent (Lamb et al., 1984). The adsorbent tube sampling technique was used for α-pinene measurements to avoid problems of bag leakage and contamination encountered during a Pennsylvania field study (Lamb et al., 1985).

Energy Balance/Bowen Ratio Approach (EBBR). HC fluxes can be calculated from surface layer theory, where the flux is given as $F = - K_z \cdot (dC/dz)$. The HC flux, however, can be estimated without the explicit need to determine the turbulent diffusivity (K_z). This unique method is based on partitioning the radiant energy incident upon the forest into various

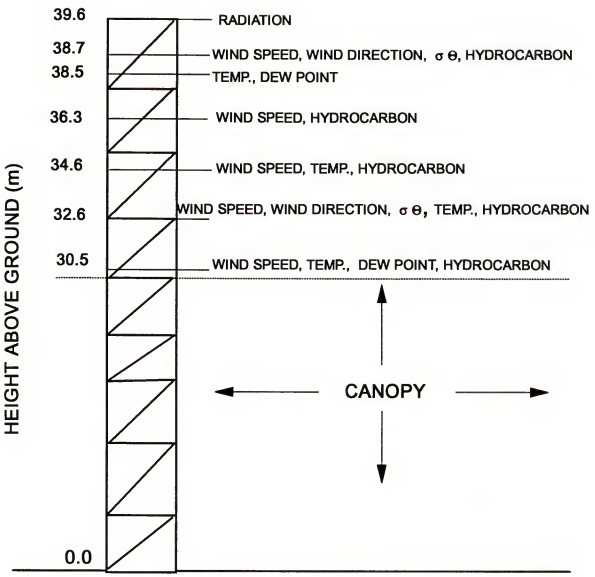


Figure 2-3. Meteorological Sensor and Hydrocarbon Sampling Locations used in the Washington Douglas Fir Forest. Source: Lamb et al., 1985

components. The Bowen ratio (H/LE) is also involved in calculation of the HC flux, where H indicates the sensible heat flux and LE the latent heat flux (Arnts et al., 1982). This method usually does not utilize bag enclosures but is extremely sensitive to measurement error.

For example, a very sophisticated micrometeorological measurement system, consisting of sampling probes and measurement sensors are located on a 25 m scaffolding tower (Figure 2-4) and analytical instrumentation contained in two vans, are used for vertical atmospheric profile measurements of water vapor, carbon dioxide, temperature, and wind speed at 18 levels within and above a loblolly pine tree forest canopy. Point measurements are taken for wind direction, atmospheric pressure, and net radiation. A sampling system to collect air samples in Teflon bags at six levels above the canopy is added for the analysis of α-pinene. Stainless steel bellows pumps withdraw air samples from existing water vapor/carbon dioxide sampling manifolds through Teflon tubing into 25 L Teflon bags (Seila et al., 1982).

The principal advantage of the EBBR method is that a total flux, which includes emissions from leaves, ground litter, and other non-leaf vegetative surfaces, is determined

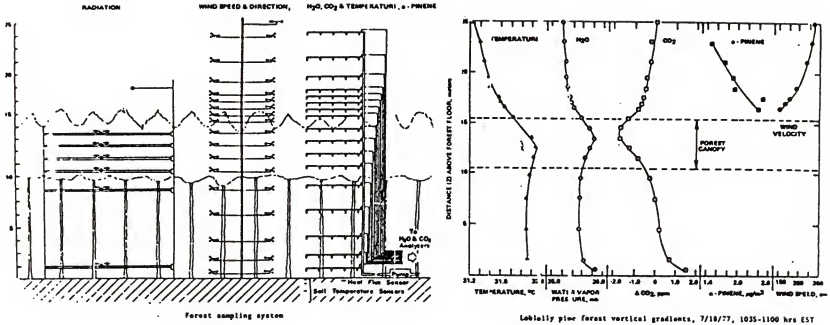


Figure 2-4. Forest Sampling System and Loblolly Pine Forest Vertical Gradients.

Source: Seila et al., 1982

directly, rather than from individual emission rates and biomass densities, both of which can have large uncertainties.

The disadvantages of this method are that it is complicated and expensive and that the analytical method for determination of hydrocarbon concentrations must be very sensitive and specific. Because of limited availability of flux estimates and the lack of simple functional relationships with environmental variables (e.g., terrain and meteorological factors), only approximate flux estimates can be made at this time (Seila et al., 1982).

Atmospheric Tracer Techniques

Sulfur Hexafluoride Tracer (SF_6) Experiments. This technique can be used as a test for enclosure methods. The procedure employs the simulation of forest emissions with an inert SF_6 tracer release and simultaneous measurements of the downwind concentration profiles of the tracer and natural HC concentrations. The flux of HCs can be calculated from the measured tracer flux and HC concentrations. This approach does not require perturbation of the vegetation nor does it rely upon precise gradient measurements (Lamb et al., 1986).

Lamb et al. (1986) applied this experimental procedure to determine isoprene emission fluxes from an isolated oak grove.

However, this approach has several distinct disadvantages.

1. The logistics of operating two simultaneous sampling sites presents problems. These problems include sample timing, instrument calibration, personal limitations, and site selection.

2. It is nearly impossible to find an ideal site for this type of study. Most sites represent compromises in that they are affected by wind shifts due to local terrain effects or weather patterns, mixing of the incoming air, and the fact that vegetation emissions are never uniform. Moreover, anthropogenic emissions invariably impact on the vegetation study area. The end result is that a large number of samples are required so that trends can be determined.

3. This procedure also suffers from the fact that biogenic hydrocarbon emissions may be depleted by atmospheric reactions occurring between the sampling points and these are not taken into account. This upwind/downwind scheme, therefore, invariably requires complicated and highly speculative modeling to estimate emission rates.

4. Rural ambient VOC levels are usually quite low and, therefore, problems of analysis and accurate quantitation are

extensive. These field programs are, consequently, very expensive by their nature.

5. This measurement approach cannot readily isolate any of the variables which might affect the determination of emission rates. Specific variables include ambient temperature, solar radiation, and relative humidity (Zimmerman, 1979a).

Tracer Model Approach. A field study was conducted to estimate the emissions of α-pinene from a pine forest without disturbing the vegetation. A tracer, sulfur hexafluoride (SF_6), was released from the forest and collected downwind in order to define the dispersive characteristics of the atmosphere. Simultaneously, α-pinene concentrations were measured both upwind and downwind of the forest. A Gaussian plume dispersion algorithm incorporating HC loss due to ozone and OH radical reactions was used to estimate α-pinene emissions (Arnts et al., 1982).

Wind speed and direction instrumentation was erected at the 35 m level. The SF6 was released at five locations intersecting the pine forest at approximately tree-top level (R1-R5). Before conducting the field study the Point Area, Line Source (PAL) dispersion model was used to (1) determine the sensitivity of concentrations from the SF_6 release points

to wind direction; (2) determine the emission rate of SF_6 that should be used during the field project and (3) demonstrate that the five projected release points of SF_6 would simulate a line source with atmospheric conditions likely to be encountered during the study. The air samplers were deployed (U1-U3, D1-D5) as deployed in Figure 2-5. They are situated in fields at distances from the tree line at least 10 times the height in the upwind forest. These criteria allow for sufficient vertical mixing, and thus minimize any concentration gradients caused by unpredictable sub-canopy mixing. Samplers are also placed on a look-out tower at three elevations. All air samples are collected in 20 L (2 mil thick) polyvinyl fluoride (Tedlar, DuPont) bags. Bags are vacuum checked for leaks and purged three times with helium before use. To minimize loss of terpenes due to reaction with ozone after collection, the sample bags (U1-U3, T1, T3 and D3) are pre-spiked with a small quantity of nitric oxide. Additionally, these bags are covered with black polyethylene to prevent post-collection photochemical reactions (Arnts et al, 1982).

This approach does not require disturbance of the vegetation nor does it rely upon precise gradient

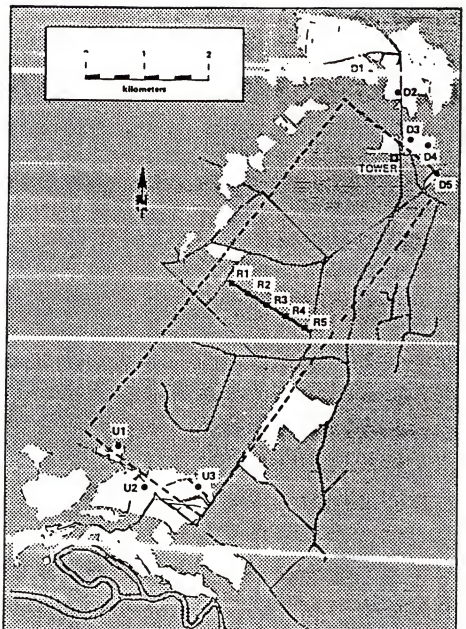


Figure 2-5. Area of Study. Shaded Area is Pine Forest; White Areas are Open Field. U1-3 are Upwind Hydrocarbon Samplers. R1-5 are Sulfur Hexafluoride Release Towers and D1-D5 are Downwind SF_6 Samplers.
Source: Arnts et al., 1982

measurements. The Tracer Model approach shares similar disadvantages outlined for the other tracer experiments discussed above.

Multi-Port Sampling Device (MPSD) Approach

The MPSD approach allows for continuous, non-destructive measurement of total, non-methane hydrocarbons and CO_2 flux from needles of grown trees. Glass tubes are positioned to contain 10 needle fascicles on each of three trees per treatment. The tubes are connected by Teflon tubing to manifolds through which air can be continuously drawn. This provides a "pooled" sample for each tree and allows for gaseous treatments of elevated ozone and CO_2 to continue throughout sampling (Johnson and Allen, personal communication).

Environmental Gas Exchange Chamber

Gas Exchange Chamber. A dynamic mass-balance gas-exchange chamber has been used to determine monoterpene emission, transpiration, and photosynthetic rates (Figure 2-6). The gas-exchange chamber was housed within a controlled environmental chamber, which have regulated light intensity and cooling. Light intensity and duration, leaf or air temperature, dew point, and CO_2 concentration were controlled

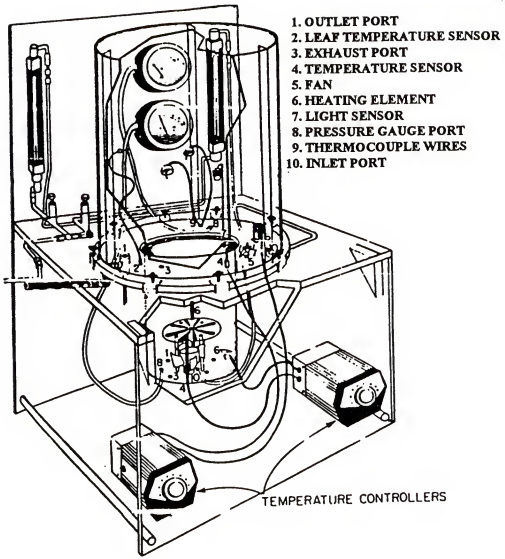


Figure 2-6. Plant Gas-Exchange Chamber with the Major Components Identified. The Volume of the Upper and Lower Chambers is 44 and 11 Liters, Respectively.
Source: Tingey et al., 1979

within the gas-exchange chamber. In addition, biological factors such as plant species, plant water status, and plant nutrition were also controlled. Ambient air was pumped through an Aadco pure-air generator to remove HC's and CO_2 and to lower the dew point. Carbon dioxide and water vapor were added back into the air stream to obtain the desired levels within the gas-exchange chamber. The air flow at the inlet port of the chamber was monitored by a flow meter and controlled in the range from 2 to 5 L/min depending on plant size and environmental conditions. Carbon dioxide, water vapor, and hydrocarbon concentrations were measured at the inlet and outlet ports of the gas-exchange chamber, and air flow was measured at the inlet. During the experiments, the CO_2 concentration in the gas-exchange chamber was maintained at 350 μL/L $\pm$40 μL/L. The dew point of the air entering the chamber was kept constant during the experiments at approximately -3 °C to 0 °C, while the dew point of air exiting the chamber was in the range from 26 °C to 38 °C, depending upon radiation and temperature conditions. Air temperature within the gas-exchange chamber was measured with a shielded-thermocouple, and leaf temperature was measured with a thermocouple pressed against the shaded portion of a

needle or leaf at mid-canopy level. Light intensity at canopy height was measured with a Lambda instrument model LI-190SR Quantum Sensor (Tingey et al., 1979).

The gas-exchange chamber is conceptually similar to that described by Huang et al. (1975), with the mixing characteristics of a continuously stirred tank reactor (CSTR) (Rogers et al, 1977). To insure complete mixing, the gas-exchange chamber contained a fan with exterior motor and the upper chamber contained three 2.5 cm high baffles arranged equidistant around the inside walls of the chamber to promote turbulence. Air samples (20 mL) were collected from the ports of the gas-exchange chamber using 100 mL gas-tight syringes or encapsulation bags to determine HC concentrations. Gaseous fluxes (J) from gas-exchange chamber data are calculated using the following equation:

$$J = \Delta C \cdot (F/P) \qquad (4)$$

where: ΔC = change in concentration of HC in the gas on passage through the chamber

F = rate of air flow through the chamber

P = leaf area or leaf weight

Gas Exchange System incorporating a GC. Monson and Fall (1989) used a gas exchange system incorporating a gas

chromatograph (GC) to measure isoprene emissions from Aspen leaves. Gas exchange measurements were conducted with an open infrared gas-analysis system. Single, attached leaves were sealed into a temperature-controlled, nickel-plated cuvette with a glass lid. Temperature was controlled by flowing water from a temperature-regulated water bath through the walls and floor of the chamber. Leaf temperatures were monitored with a 0.1 mm diameter copper-constantan thermocouple pressed to the underside of the leaf. Two small fans in the cuvette provided air mixing over the leaf surfaces with leaf boundary-layer conductances ranging from 1.5 to 2.0 mol/m^2-sec, depending upon the species (Monson et al., 1986). The gas exchange system described above, including the leaf cuvette, was used in this experiment. A gas stream was withdrawn from the outlet of the leaf cuvette at a constant flow of approximately 80 mL/min. This outlet air was transported through Teflon tubing into a drying-tube that was maintained at -80 °C in a dry ice bath. With most of the water removed, 186 standard mL samples were withdrawn by opening a stainless steel valve, allowing the sample to flow through a Teflon capillary sample loop submerged in liquid nitrogen and into a previously evacuated 7.7 L calibrated stainless steel flask.

Removal of most of the water from the sample prevented freeze-up of the sample in the loop used for cryogenic preconcentration (Monson and Fall, 1989).

Loreto and Sharkey (1990), also, used a gas-exchange system incorporating a GC to study photosynthesis and isoprene emission from Quercus rubra L. Single oak leaves were clamped in an aluminum cuvette with glass windows at the top and bottom surfaces. For isoprene measurements, some of the air leaving the cuvette was dehumidified through a dry-ice trap and then passed through a 0.5 mL autoinjector loop. A six-way valve automatically switched the loop into the carrier gas stream of the GC analytical system.

Sampling Approaches in Characterizing and Estimating Airborne Monoterpenes

There are several different types of ambient air sampling approaches that have been employed for monoterpene measurements. About 21 representative studies that have previously been conducted since the 1960's were surveyed.

Reinhold et al., (1965) carried out in-situ direct injection of ambient air to a GC in a mobile laboratory. They suggested that direct injection of ambient air samples containing ppbv levels of HCs produced measurable responses in

sensitive GC systems. Since that time, it has been recognized that analytical determinations of ambient monoterpene levels using GC systems in non-industrial environments require a preconcentration step for most collection techniques instead of directly using the levels found in Tedlar/Teflon bags or ambient air.

Methods commonly used for preconcentration are absorption in solvents, cryogenic trapping or adsorption on solid sorbents. In general, one of two practical approaches has been employed for sample preconcentration. Cryogenic trapping or gas/solid adsorption are preferred for preconcentrating volatile organics in ambient air.

Whitby and Coffey (1977) attempted to preconcentrate hydrocarbons using a cryogenic cold trap with a small loop connected to a GC system in a field laboratory. Since it is very expensive to use a mobile laboratory containing complete analytical systems and accessories, containment of air samples before preconcentration and analysis became necessary.

There are several methods for capturing air samples. Bag sampling using a vacuum pump with Teflon and stainless steel exposed parts has been a traditional and simple procedure for ambient air sampling (Lonneman et al., 1978; Arnts and Meeks,

1981; Zimmermann et al., 1988). Evacuated canisters were used for collecting ambient air samples by expansion into an evacuated container (Whitby and Coffey , 1977). Seila and Lonneman (1988) used electropolished, 6 L stainless steel spherical flasks for this application (Khalil and Rasmussen, 1992). Solid sorbents have been widely used for collection of ambient monoterpenes or HCs for emission rate sampling since the 1970's. Twelve out of the 21 representative research groups surveyed have used this solid adsorption approach.

Initial development of stainless steel canisters for routine collection of air samples was carried out at Washington State University in a program under the direction of Dr. Rei Rasmussen (McClenny et al., 1991). In recent studies it was shown that storage of monoterpenes in conditioned stainless steel canisters can be problematic due to the disappearance of the hydrocarbon with time (Winer et al., 1989; Apel and Calvert, 1994). However, two method intercomparison experiments have been conducted that provide support for the stability of terpenes in a stainless steel canister. Clearly, the best way to verify the reliability and accuracy of the sampling procedure is to compare terpene concentrations from samples collected simultaneously by two

different techniques. Holdren (1979) used two sampling methods (6-L stainless steel evacuated canisters and 60/80 mesh Tenax adsorbent) to collect and analyze ambient air samples. The comparative results obtained from using solid adsorbent collection techniques and standard canister collection techniques, with the latter procedure followed by cryogenic concentration, are presented in Table 2-1. For the two sampling periods identified in the table, canisters were purged and filled to 0.28×10^5 N/m^2, while at the same time, 100 mL of ambient forest air was passed through a tube containing Tenax-GC adsorbent. As the results in Table 2-1 imply, terpene concentrations determined from 100 mL of canister air agree very closely with the values obtained by thermal desorption of the Tenax sample (Holdren et al., 1979).

Cryogenic trapping has been demonstrated to provide excellent recovery and precision for a number of volatile organic compounds, but the method is somewhat inconvenient when used in the field because of the complexity and size of the apparatus involved. However, solid adsorbents can be conveniently transported to the field for sampling and returned to the laboratory for analysis. Unfortunately, none

Table 2-1. Tenax versus Canister Collection.

Date	α-pinene	β-pinene	Δ^3-carene	Limonene
Nov. 16, 1976	pptv	pptv	pptv	pptv
canister	30	40	<10	<10
canister	40	40	<10	<10
Tenax	50	50	<10	<10
Tenax	25	40	<10	<10
Nov. 19, 1976	pptv	pptv	pptv	pptv
canister	120	200	30	20
canister	110	200	30	10
Tenax	130	190	40	10

Source: Holdren et al. (1979)

of the existing solid adsorbents show recoveries comparable to cryogenic trapping techniques for a wide range of components. By far the most widely employed adsorbent for volatile organic compounds is Tenax-GC. Tenax has the advantage of good thermal stability which allows for efficient desorption of higher boiling point hydrocarbons (e.g., C-6 to C-12) during the analysis step. A primary limitation in the use of Tenax is the low retention volume for highly volatile compounds (e.g., vinyl chloride) (Riggin and Markle, 1986).

Choice of Sorbents

Physical adsorption of trace atmospheric constituents on the surfaces of different sampling systems has long been recognized as a factor contributing to apparent losses of some organic compounds during sample storage and collection (Isidorov et al., 1985).

Comparison of Carbochrome and Tenax-GC. Sorbents intended for use in concentration of components in volatile HC emissions from plants should ensure complete capture of a wide group of organic components and their complete recovery without isomerization reactions and losses due to irreversible sorption (Isidorov et al., 1985). Carbochrome and Tenax-GC porous polymer have been used as such sorbents. The sorption

ability was determined by injection of fixed volumes of urban air or artificial gas mixtures with an admixture of organic compounds into sorbent tubes connected in series and their subsequent separate desorptions allowed for determination of individual values for maximum allowable injection volume. Experiments showed that tubes with 0.6-0.7 g of Tenax-GC completely trap terpene HCs from an air volume greater than 15 L (Isidorov et al., 1985). However, breakthrough of lower M.W. HCs and their oxygen-containing derivatives was observed with injection volumes as low as 0.5 L (Isidorov et al., 1985). Hence, Tenax-GC adsorption can be applied to the determination of terpene components in large volume air samples, but is unsuitable for the quantitative trapping of more volatile components. Carbochrome exhibited a better sorption capacity. HCs with more than four carbon atoms, as well as their derivatives, are captured without breakthrough from air samples with volumes greater than 8 L.

One of the most important stages of HC analysis using sorbents is thermal desorption, because terpene and other reactive/unstable HCs can undergo transformations on the heated surface of the sorbent.

A special investigation (Isidorov et al., 1985) showed that even for a short desorption time in a He flow at 400 °C, over 60% of α- and β-pinenes are lost from Carbochrome as a result of isomerization, polymerization and dehydration, with the formation of p-cymene. A decrease in desorption temperature to 250 °C makes it possible to prevent isomerization, but in this case a large amount of p-cymene is formed. The results of an analysis of a mixture of terpenes and n-alkanes after their desorption at 300 °C are presented in Table 2-2. These data were obtained by averaging the results of five to seven experiments. A comparison of relative compositions of the artificial mixture and of the HCs desorbed by H_2 from Carbochrome and by He from Tenax showed that α- and β-pinenes are completely recovered within experimental error and that dehydration processes are negligibly low. The results show that under these conditions both sorbents may be used in the analysis of VOCs from vegetative emissions.

Comparison of Tenax-TA and Carbotrap Sorbents. Frequently, activated charcoal is used as an adsorbent for hydrocarbons. Due to its high surface activity, however, chemical reactions may occur during storage of the samples.

Table 2-2. Desorption of Terpene Hydrocarbons at 300°C.

Components of the Mixture	Composition of the initial hydrocarbon mixture relative to n-nonane	Composition of desorbed hydrocarbons relative n-nonane	
		Carbochrome*	Tenax GC+
n-Nonane	1.00	1.00	1.00
α-Pinene	5.3±0.2	5.6±0.2	5.3±0.3
Camphene	0.15±0.03	0.22±0.03	0.16±0.03
n-Decane	1.0±0.1	1.0±0.1	1.0±0.1
β-Pinene	0.7±0.1	0.6±0.1	0.6±0.1
3-Carene	1.3±0.2	0.9±0.1	1.2±0.4
Limonene	0.8±0.1	0.7±0.1	0.8±0.2
p-Cymene	0.2±0.1	0.3±0.1	0.2±0.1
n-Undecane	1.7±0.2	1.7±0.2	1.7±0.4

note: * Desorption in hydrogen flow, 6 mL/min.
+ Desorption in helium flow, 1.2 mL/min.
Source: Isidorov et al., 1985

Often very low recoveries are found, in the ppbv range, because of partial decomposition of the sampled compounds and strong adsorptive behavior. On the other hand, polymeric adsorption materials are less reactive or may even be inert, but have lower retention volumes for VOCs. The resulting loss of sensitivity, compared to activated charcoal, can be overcome by thermal desorption, where the sample is directly transferred to the separation column. Whereas short, open capillary tubes with an activated charcoal layer can be thermally desorbed with little difficult and expense, inert polymer sorbents require adsorption tubes with larger dimensions and a greater gas volume for desorption (Rothweiler et al., 1991).

Tenax is an adsorbent widely used in the field for air analysis. It is claimed to be inert with respect to sampled compounds. No chemical reactions have been observed in the presence of substantial amounts of ozone. On the other hand, Rothweiler et al. (1986) found nitro-derivative artifacts when desorbing polycyclic aromatic hydrocarbons (PAH) in the presence of nitric oxides. Furthermore, in the presence of reactive hydrocarbon compounds, small amounts of benzaldehyde,

acetophenone and phenol were observed to be released from the adsorbent.

Tenax-TA is a further development of Tenax-GC, porous polymer sorbent. It can be cleaned simply by heating in an inert gas flow, is stable up to 280 °C and produces less artifacts than Tenax-GC. Carbotrap is a very pure graphitized carbon black. Its adsorptive capacities are based on London dispersion forces (Supelco, 1992). It can easily be thermally cleaned in an inert gas flow. Carbotrap is said to be free of contaminants and not susceptible to sorbent degradation. Nevertheless, tiny impurities in the adsorbent could act as specific active sites. Reaction products have not been reported so far, but Carbotrap has not been investigated as thoroughly as Tenax (Rothweiler et al., 1991). Trace amounts of VOCs present in air can be determined quantitatively by adsorption and concentration on Tenax-TA or Carbotrap materials followed by thermal desorption. A comparison of these sorbents suggests that Tenax-TA is more inert toward the various HC compounds tested, while terpenes and aldehydes show some reactivity when sorbed on Carbotrap. Compounds with higher boiling points up to 270 °C could be quantitatively desorbed from Tenax-TA but not from Carbotrap. Substantial

losses of adsorbates have been attributed to breakthrough. Such losses were observed on both adsorbents for very volatile organic compounds and various polar VOCs. Alpha-pinene recovery on Tenax-TA was 71.2 ± 18.8%, whereas for Carbotrap the recovery was only 1.8 ± 0.7%. Air sampling volumes for this recovery study were 1 liter, and three measurements were made for each sample. Alpha-pinene and aldehydes showed some reactivity on Carbotrap. Therefore, for the analysis of complete VOC composition in an air sample, additional methods and adsorbents have to be used. Other carbonaceous adsorbents (Carbosieve S-III, Carboxen 563 and 564) have been studied for use in collecting very volatile organic compounds, and other polymeric adsorbents such as Chromosorb 106, Porapak Q and Porapak S are under investigation. However, the cleaning procedure for the latter adsorbents is time - and material-consuming and the blanks are apparently not as clean as those obtained with Tenax TA and Carbotrap (Rothweiler et al., 1991).

Hydrocarbon Analysis and Calibration Techniques

Hydrocarbon Analysis Approaches

The need to speciate and measure low levels of VOCs (e.g., monoterpenes, isoprene) has increased over the last several years. Detection, identification, quantification of organic compounds at low levels (ppbv or pptv) are difficult using a gas chromatograph (GC) equipped with a flame ionization detector (FID) or any other detectors. Instrument response can be increased by sampling larger volumes; however, chromatographic peak shapes and analytical precision are compromised when more than 10 mL of a gas sample is injected. Because of the low concentration levels of organics in air, the response is poor and some compounds cannot be detected; therefore, it is necessary to increase the amount of organic material injected onto the chromatographic column without increasing the gas sample volume (Rhoderick and Miller, 1990). The use of cryogenic trapping to concentrate VOCs prior to analysis has been established as a proven technique for VOC monitoring. The temperature of the trap is below the condensation temperatures for trace VOCs but above the condensation temperatures for major constituents of ambient

air. After collection, the trap is rapidly heated, the VOCs are instantaneously vaporized onto the column of a GC system. An alternative trapping method involves the use of adsorbent materials to collect VOCs at ambient temperatures. Popular adsorbents include Tenax-TA, silica gel, carbon molecular sieves, and activated charcoal. Tenax is a fairly weak adsorbent and is preferred for certain compounds (e.g., monoterpenes) with boiling points above 100 °C (Brown et al., 1992). Desorption is accomplished by elevating the trap temperature prior to GC analysis. Deficiencies reported with mono-adsorbent traps are their inability to completely collect and/or desorb samples possessing a wide range of molecular weights, and the presence of artifact materials. By using selected adsorbents in a multi-bed trap configuration, collection devices can be tuned to capture a wide range of compounds with minimal artifact interferences (Pollack et al., 1991).

It was found from a literature review that different research groups have used different analytical instrument configurations. Most research groups have used GC-FID and/or GC-MS systems with glass or fused-silica capillary columns.

Calibration Techniques

Static dilution (Rasmussen, 1964; Morris et al., 1983), reference materials (Zimmermann, 1979a; Knoppel et al., 1982; Juttner et al, 1988), evacuation and pressurization (Whitby et al., 1977), diffusion tube (Riba et al., 1987; Arnts et al., 1981), and solvent (e.g., methanol) dilution (Winer et al., 1983; Helmig et al., 1992; Arey et al., 1990) approaches have been used for making calibration standards of monoterpene HCs during the last thirty years.

Static Dilution Method. GC calibration standards are obtained by injecting 1μL samples of the liquid material into two liter flasks, filled with pure air. The air mixture is allowed to come to an equilibrium. Gas tight syringe samples of the HC air mixture are extracted and injected to the GC column (Rasmussen, 1964).

Reference Material Method. It is assumed that all VOCs measured have an FID response equal to the FID response for neo-hexane (Zimmermann, 1979a). The GCs are routinely calibrated using a neo-hexane standard (0.209 ppmv) prepared by Scott Research Inc.

Evacuation and Pressurization Method. Calibration samples were prepared by injecting liquid terpene samples into

evacuated glass cylinders and then pressurizing the cylinder with nitrogen. Successive dilutions were made to provide HC calibration concentrations in the 50 to 1000 $\mu g/m^3$ range (Whitby et al, 1977).

Solvent Dilution Method. Calibration samples for quantitative analyses were prepared by spiking Tenax cartridges with 1 μL of standard solutions in methanol (Optima, Fisher Scientific) followed by flushing the cartridges with 100 mL pure Helium to elute the solvent (Helmig et al., 1992).

Diffusion Tube Method. A diffusion tube was used for generating standard gas mixtures. The thermostat bath was maintained at 20±0.2 °C (Riba et al., 1983). This is the most widely used dynamic flow method based on the effusion of molecules of the component to be measured into a flowing stream of gas. The method is reliable and suitable for volatile hydrocarbons under both laboratory and field conditions. The only disadvantage of this method is that the initial cost is high (Namiesnik, 1984).

Air Quality Measurements

Routine air quality, ozone and nitrogen oxides measurements (O_3, NO/NO_x), and micrometeorological monitoring

activities have been carried out at the Austin Cary Forest site since 1988. Although this site is a cleared rural area surrounded by pine trees, the daily maximum hourly average ozone concentrations have frequently exceeded 70 parts per billion (ppbv) and occasionally levels near 100 ppbv have been reported (Allen, 1991).

Air quality standards were established by U.S. EPA in 1971 to prevent or minimize the risk of adverse effects of exposure to air pollution on human health, vegetation, and materials. In the United States, public health and environmental ambient air standards for ozone currently are set at 120 ppbv. Suggestions have been made in the literature, however, that the current standard may not be appropriate for protecting vegetation from ozone exposures (Lefohn et al., 1991). For instance, Guderian et al. (1985) recommended that sensitive vegetation should not be exposed for more than 4 consecutive hours to hourly average concentrations of 50 ppbv.

Seasonal variations in hourly ozone averages, and daily averages/maximums for 1989, are shown in Figures 2-7 and 2-8, respectively, for the Cary Forest site. The daily maximum concentrations of ozone occurred between 1 and 3 p.m. (local

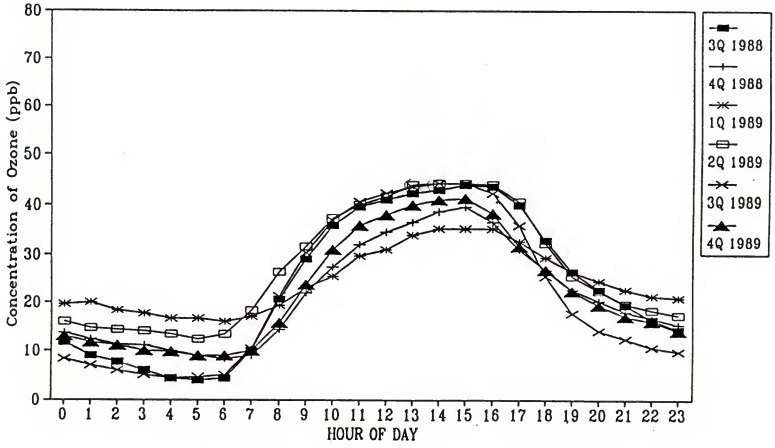


Figure 2-7. Seasonal Variations in Diurnal Ozone Concentrations at Cary Forest FL in 1988-89.

Source: Allen and Sutton, 1991

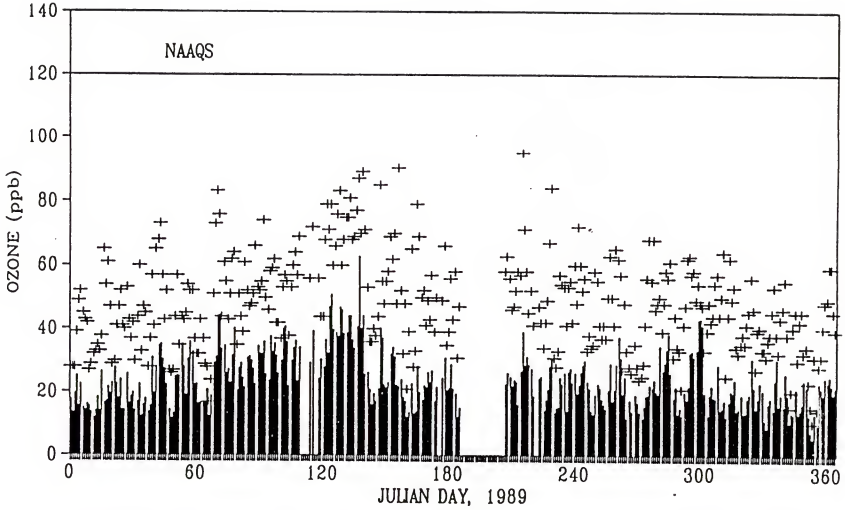


Figure 2-8. Ozone Daily Averages (bars) and Maximums (crosses) for cary Forest, FL in 1989. FL in 1988-89.

Source: Allen and Sutton, 1991

standard time). Concentrations at night were very low compared to those in the daytime (Figure 2-7). It is also readily apparent from Figure 2-8 that the maximum values for ozone occur during the spring quarter (April to June). Spring is the most active period in the growing season for vegetation. More photosynthates are available; therefore, more plant-emitted NMHCs might be released into the Cary Forest airshed. Spring conditions at this rural site can also be considered to be part of the dry season (Allen, 1991), hence this period can be considered favorable for photochemical reaction because ozone is usually negatively correlated with relative humidity (Chung et al., 1986).

If photochemical reactions significantly contribute to the observation of ozone in pine forests, then the role of natural NMHCs would be critical since the concentration levels of NO and NO_2 are very low compared to those for urban areas. Allen (1991), however, has reported that Cary forest soils are a primary source of NO, presumably due to soil microbiological processes (Kardono and Allen, 1990). It is important, therefore, under these circumstances to realize that the main source of NO could be at ground level, whereas the sampling port for air quality measurements (e.g., NO, O_3) is located at

4 m above ground level. It is possible, therefore, that ambient levels of NO near the ground are underestimated at the Cary Forest site by the ambient air monitoring used.

Neither routine nor periodic measurements of natural hydrocarbons have been conducted at the Cary Forest site. Although natural hydrocarbons might be critically important precursors of ozone, it has been difficult to explain high local levels of rural ozone because the overall mechanism of ozone formation in the atmosphere is complicated. It appears, therefore, to be appropriate and meaningful to study the effects of natural HC emissions on the rural environment by continuously monitoring local meteorological and air quality variables in conjunction with HC emission studies and ambient air studies. For instance, the observed relationships between natural HCs and ozone or its precursors in this rural area could provide significant basic information necessary to assess the contribution of biogenic emissions to deterioration of rural air quality (i.e., ozone production).

CHAPTER 3
RESEARCH METHODOLOGY

Experimental Methods

General Description of Field Site and Laboratory Systems

The research field site is located at the Austin Cary Forest, within a 2 hectare cleared area surrounded by commercial pine plantations. This rural site is located approximately 15 kilometers NE of the downtown business district of Gainesville, home of the University of Florida (UF), in the north central region of the Florida peninsula. At this site, routine air quality, meteorology, acid deposition monitoring activities, and open-top chamber studies have been conducted by UF scientists since 1988.

Local sources of criteria pollutants (SO_2,NO/NO_2,O_3) within a 10 km radius, which may influence air quality at the Cary Forest, FL monitoring site are as follows. A heavily traveled highway (State Route 24) is located, at its nearest

point, approximately 0.4 km (0.25 miles) to the NW (315° bearing) of the monitoring shelter. Otherwise, only lightly traveled minor paved roads are located within a 5 km radius. Principal stationary sources of nitrogen and sulfur oxides within a 20 km radius of the site include Gainesville Regional Utilities, Deerhaven coal burning and Skelly oil burning power plants located approximately 16 km to the west and southwest, respectively. Major regional industrial sources include the Georgia Pacific paper pulp mill at Palatka, located approximately 60 km (36 miles) to the east (95° bearing) and distant power plants, chemical plants and pulp mills in Jacksonville located about 90 km (56 miles) to the northeast.

At the study site, an insulated, air-conditioned equipment shelter is used to house meteorological and air quality instrumentation. Wind speed and wind direction are routinely measured at 10 m above ground level on a tilt-down tower. Air temperatures are measured at 8 m and 1 m and relative humidity at 8 m elevation on the same tower. Barometric pressure is measured outside the shelter at 1.5 m above ground. Ambient air (for air quality monitoring; see Figure 3-1) is sampled at 1.5 m above the roof of the shelter (4 m above ground level). A field data acquisition system

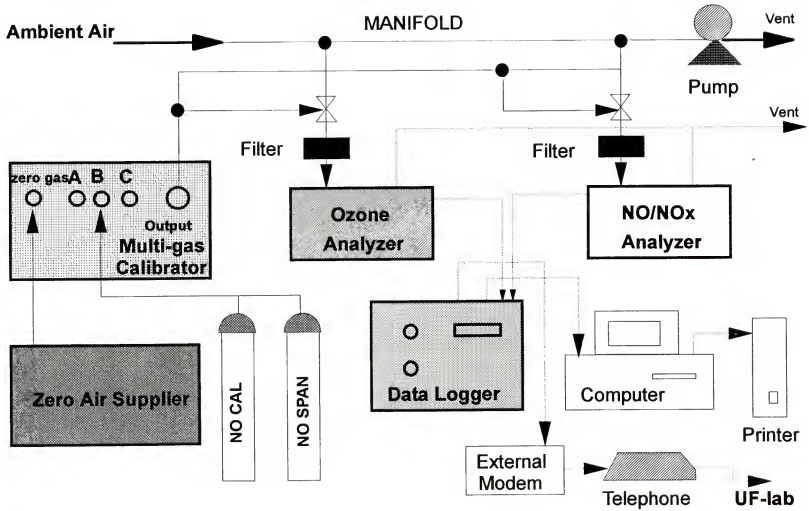


Figure 3-1. Flow Diagram for Continuous Air Quality Monitoring at Cary Forest Field Site.

(DAS) consists of an Odessa Model DSM 3260 datalogger and an IBM-compatible personal computer (PC). The datalogger is used to acquire, average, store and communicate data received from all continuous sensors (air quality analyzers and meteorological instruments). Stored data is accessible directly via the on-site PC or by polling the datalogger remotely, through an external telephone modem (Allen, 1991).

Field sampling studies of hydrocarbon emissions were carried out on loblolly and slash pine saplings growing at the Cary Forest field site. These studies were in support of UF School of Forest Resources and Conservation global climatic change research on pine tree growth and emissions conducted by Dr. J. Johnson. The layout of the sampling site is shown in Figure 3-2.

Ambient air and tree emission samples collected at the field site were analyzed at the Air Pollution Laboratories in Black Hall at UF (UFAPL). The UFAPL contains two research gas chromatographs (GCs). One GC (Perkin Elmer Model 8500) is fitted with flame ionization and electron capture detectors (FID/ECD)and is used specifically for separation and quantification of hydrocarbons. The other system is a GC-ITD (Perkin Elmer Model 8420, Ion Trap Detector(ITD): Finnegan)

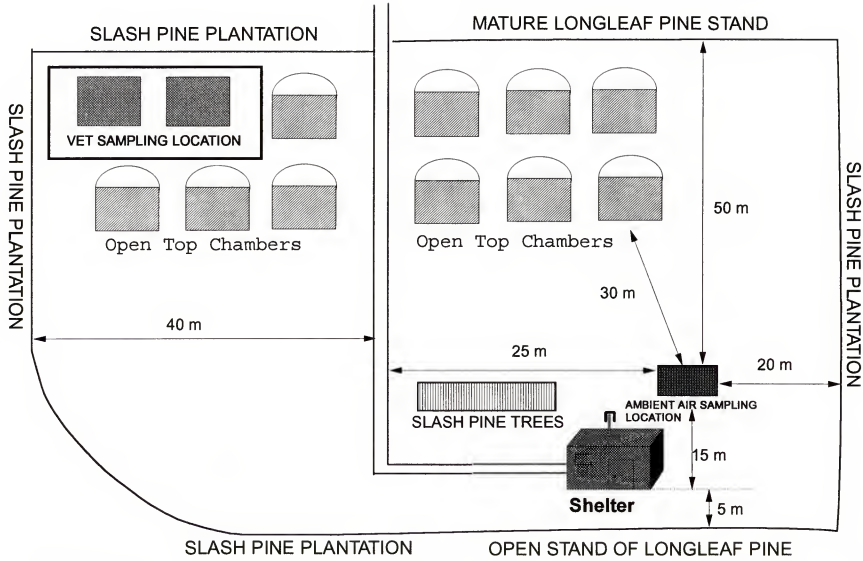


Figure 3-2. Layout of Cary Forest Site Showing Ambient and Vegetation Enclosure Technique (VET) Sampling Locations.

system for the separation and quantification of biogenic NMHCs. Both the GC-ITD and GC-FID systems are equipped with automated thermal desorption transfer and injection systems (Model 5010GT, Tekmar, Cincinnati, OH) enabling automated transfer of VOCs from sorbent traps, Tedlar bags, evacuated canisters and gas-tight syringes to the GC columns.

Development of Analytical Methods

Monoterpenes hydrocarbons ($C_{10}H_{16}$) are unsaturated natural volatile organics which have been found in the planetary boundary layer and the free troposphere. These compounds are highly viscous in the liquid phase and are unstable in air at higher temperatures (≥200°C) (Beynon et al., 1968). As mentioned earlier, it is essential to preconcentrate biogenic hydrocarbon in air samples before injection to the GC column. In this research, a concentration was achieved by adsorption on Tenax-TA sorbent followed by use of an automated desorbing and cryogenic focusing system (Tekmar, Model 5010-GT Automatic Desorber). Conditions for sampling and analysis were specifically developed, and used for monoterpene measurements.

Both the GC-ITD and GC-FID analytical systems were equipped with Tekmar Model 5010 sample introduction systems

enabling automated transfer of VOCs from sorbent traps or Tedlar bags to the GC, as shown in Figure 3-3. Because the same source (manufacturer) and similar models of gas chromatographs (Perkin Elmer, GC-8420 and GC-8500) were selected for use, almost identical GC capillary columns were installed so that the same analysis parameters could be used in both systems (GC/ITD/Tekmar and GC/FID/Tekmar). These similarity in analytical systems made it possible to easily compare and interpret the mass spectrometric and flame ionization chromatograms acquired from both systems. More specific details of the configurations and operating conditions for the GC systems are provided in Table 3-1.

One of the early analytical problems encountered using the Tekmar thermal desorption system was the influence of carrier gas (He) purity. Because a cryogenic focusing system was used, a very high purity carrier gas was needed. It was found that impurities in the carrier gas accumulated with the sample in the cryofocusing procedures in transferring samples from sorbent tubes to the GC column. Consequently, an improved gas cleaning system incorporating an additional hydrocarbon trap was set up as shown in Figure 3-3. This system was tested and it was shown that impurities were not

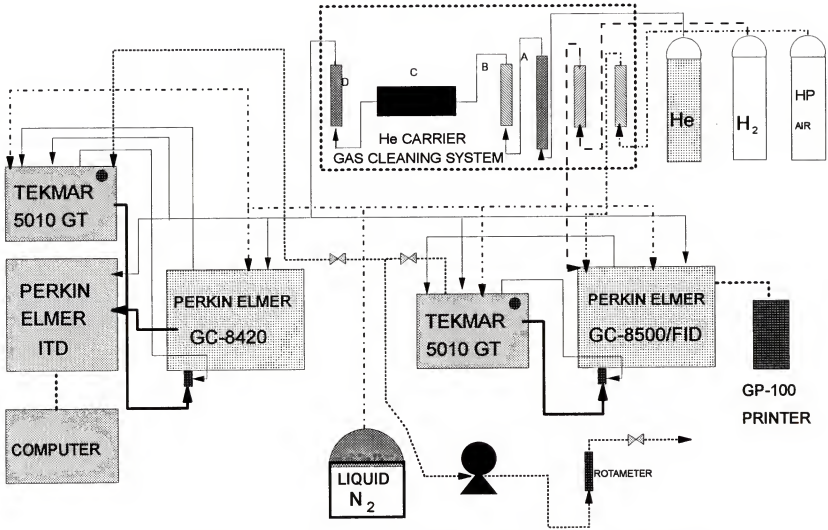


Figure 3-3. Analytical Systems Configurations for Qualification and Quantification of Hydrocarbons.

Table 3-1 GC configurations and operating conditions

GC Model	PE 8500	PE 8420
Column type	J&W Fused Silica Megabore Liquid Phase, DB-5	J&W Fused Silica Megabore Liquid Phase, DB-5
Film thickness	1.5 μm	1.0 μm
Dimension	30 m x 0.536 mm	29.5 m x 0.32 mm
He flow rate	4.4 ml/min @ 200°C	0.98 ml/min @ 200°C
He flow velocity	32.5 cm/sec @ 200°C	20.3 cm/sec @ 200°C
Detector	FID	ITD
He pressure	6.0 psig	12.0 psig
Injection T (°C)	100	100
Detector T (°C)	225	200 (Transfer line)
Air flow	410 ml/min	-
H_2 flow	38 ml/min	-

detectable at the conditions employed. Carrier gas purification was by a Molecular Sieve 5A trap (#2-0619, Supelco, Bellefonte, PA), trap (A), that removed excessive moisture and heavy hydrocarbons from the carrier gas (He). Activated charcoal (Supelpure-HC trap, #2-2446, Supelco), trap (B), was used to adsorb hydrocarbons and other contaminants. A high capacity gas purifier tube (#2-3802, Supelco), trap (C), heated inside an oven, was used to remove oxygen and water vapor, by reaction with the gettering material in the tube. An OMI indicating purifier (#2-3906, Supelco), trap (D), simultaneously removed oxygen, water vapor, carbon monoxide, carbon dioxide, most sulfur compounds, most halogen compounds, alcohols, and phenols, to less than 10 ppbv. Because as little as 1 ppmv of oxygen or moisture will change the indicating resin from black to brown, the color change was used to provide a visual indication of the purification system effectiveness.

In the early stages of this study, it was found that the Tekmar thermal desorption system decomposed syringe-injected monoterpenes when EPA default operating parameters were used. It was necessary, therefore, to adjust the recommended Tekmar operating conditions to eliminate this problem. Extensive

testing was carried out to resolve the terpene thermal decomposition problem and develop optimal conditions for handling monoterpenes (see Table 3-2). Decomposition of the biogenic hydrocarbons was found to be due to: use of an inappropriate desorption flow rate; unsuitable desorption temperature conditions, and the use of stainless steel (metal) tubes as sorbent containers.

Initially, the EPA default desorb temperature of 190°C was used in conjunction with a 5 minute desorb time, however, these conditions caused incomplete desorption of monoterpenes from Tenax sorbent. When a mixture of the same amounts of α-pinene, β-pinene, d-limonene was injected into a GC column at the predetermined (EPA default) Tekmar desorb conditions, the GC peak areas (i.e., FID response) for these compounds were considerably different, due to terpene losses and residuals retained by the Tenax sorbent. The desorb temperature (190°C) was increased to 225°C and the desorb time increased to 8 minutes. With these modified thermal desorb conditions, it was found that no measurable terpene residuals were left on the Tenax sorbent and the FID sensitivities for the same amount of the three terpene compounds tested were very similar.

Table 3-2. EPA default and optimal recommended operating conditions for transfer of biogenic hydrocarbons to GC systems using Tekmar 5010 thermal desorption systems.

Values	EPA Default values	Optimal values
Purge flow (mL/min)	10	20
Purge time (min)	5	8
Desorb flow (mL/min)	10	20
Desorb time (min)	5	8
Desorb temperature (°C)	190	225
Valve temperature (°C)	270	175
Cryo 1 and Cryo 2 (°C)	-150	-130
Cryo 1 heating temperature (°C)	250	200
Sorbent container	stainless steel	glass tube
Transfer line temperature (°C)	210	175
Cryo 2 injector (°C)	210	175

From studies of Tenax sorbent in stainless steel and glass sampling tubes it was determined that adsorption of monoterpene hydrocarbons on Tenax-TA (60/80 mesh, Alltech, Deerfield,IL) in a glass tube container was the most reproducible and efficient method for the recovery and analysis of monoterpene hydrocarbons. This observation was particularly true when these sampling tubes were used in conjunction with a commercial thermal desorption and cryofocusing system (Tekmar 5010GT) coupled to a GC.

Monoterpene hydrocarbon collection sampling tubes were prepared by filling individual pyrex glass tubes (o.d. 1.27 x 18.1 cm long) (Southern Scientific, Micanopy, FL) with about 900 mg of Tenax-TA held in place with silanized glass wool (Supelco, Bellefonte, PA). A simple and economic sorbent tube purging system, which can hold up to 6 tubes at a time, was designed, constructed and tested in-house. The sample tubes were conditioned for at least 8 hours in an oven at 250°C during which time they were flushed with nitrogen gas (Prepurified grade, Bitech, Tampa, FL). The preconditioned sample tubes, were then individually inserted into the Tekmar desorber system oven. The tube was purged for 5 minutes and baked at 250°C for 20 minutes. After conditioning the

sampling tube twice, it was then checked for the presence of impurities (background). The preconditioned clean sample tubes were stored in sealed trap sampling containers (#14-1463-000, Tekmar, Cincinnati, OH) during storage and transport. Sampling containers were stored in an ice-cooled insulated box during transport to and from the field site.

Biogenic hydrocarbon samples collected on these Tenax sorbent traps were desorbed and transferred to the appropriate GC system using the Tekmar Model 500GT automated thermal desorber (Figure 3-4). The sample trap was inserted and sealed in the Tekmar oven and prepurged with helium at 20 mL/min and 35°C for 8 minutes in order to remove oxygen and excess moisture. The trap was then desorbed under a flow of helium (20 mL/min) at 225°C for 8 minutes. The desorbed material was collected in a cryotrap (CRYO-1) at -130°C. The cryotrap was heated to 200°C and the trapped material was transferred through a heated (175°C) fused silica line to a second cryofocusing trap (CRYO-2) cooled to -130°C at the injector of the GC. The transfer process was allowed to proceed for 1 minute, and the sample components were focused in the second cryotrap at the head of the analytical capillary column. The sample was then instantaneously injected to the GC column by

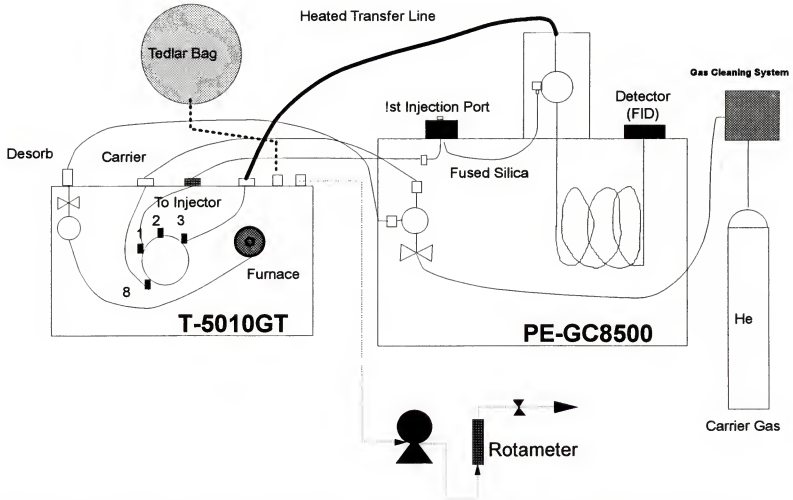


Figure 3-4. Design of a Reproducible, Versatile, & Multiple Sample Containment, Transfer & GC Introduction System.

flash heating the cryofocusing trap rapidly to 190°C. No loss of monoterpene sample was detected using known standards of terpenes for the selected conditions of sample desorption, transfer and injection employed.

The biogenic hydrocarbon sample introduction system is shown in Figure 3-4. Also, when necessary, bag or canister samples can be transferred to a cleaned Tenax trap located in the oven section of the automatic desorption system (Tekmar). A precision vacuum pump (Model #JB2N050N, Universal Electric Motor, Owosso, MI), needle valve (#SS-IRS4, Whitey, Highland Heights, OH), and rotameter (#6-1355, Brooks, Emerson Electric Co., Hatfield, PA) provide a constant flow for transfer of known volumes of samples from other types of collection systems. A sample injection port for "spiking" samples with known quantities of standard materials was built into the transfer system downstream of the Tedlar bag quick-connect attachment port.

Helium carrier gas flow rate selection for the GC systems and temperature programming of the DB-5 capillary columns were optimized for rapid, high resolution separation of biogenic hydrocarbon sample components. In the analyses of biogenic hydrocarbons using the GC-FID/ITD systems, identical

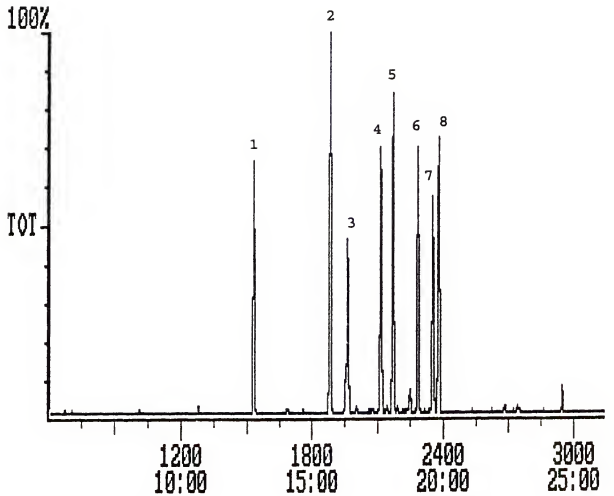
temperature programs for the column ovens were used. The DB-5 columns were held at 35°C for 2 minutes and then ramped at 4°C per minute to 120°C. At 120°C the ramp rate was increased to 14°C per minute up to 200°C and finally the columns were held at 200°C for 6 minutes.

Identification of compounds

The GC/ITD system was used to mass spectrometrically characterize and identify each of the terpene hydrocarbon compounds found in field samples. Samples of compounds under investigation were obtained from commercial sources. These compounds included isoprene (99% purity), α-pinene (99% purity), camphene (85% purity), β-pinene (99% purity), myrcene (77.2% purity), Δ^3-carene (95% purity), d-limonene (97% purity) and p-xylene (99 % purity). All of these chemicals were purchased from Aldrich Chemical Company (Milwaukee, MI). A mixture of d-limonene and β-phellandrene (60 and 40% purity respectively) was donated from Dr. Janet Arey of the University of California, Riverside. Initially, each individual organic compound was injected into the GC/ITD and GC/FID systems using the respective Tekmar thermal desorbers in order to establish relative retention times and acquire mass spectral cracking patterns. P-xylene (99% purity) was

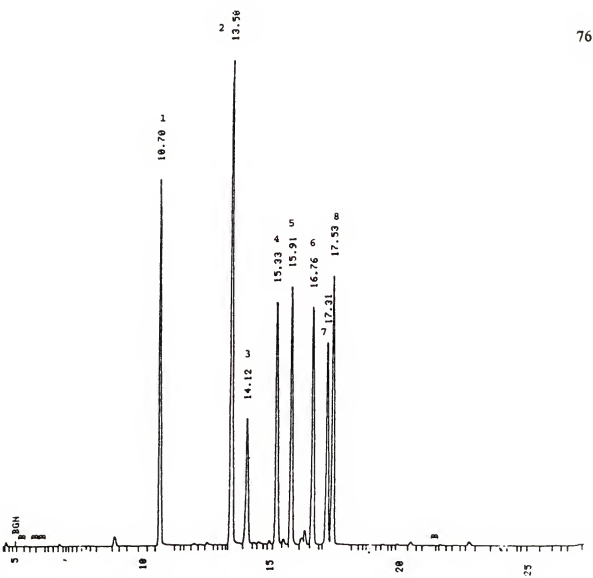
selected as an appropriate stable and reproducible, non-interactable internal standard in both laboratory studies and field sampling. Known mixtures of both p-xylene and each individual terpene were injected into the GC/MS and GC/FID systems in order to determine relative retention times and mass spectra for quality control purposes. A mixture of p-xylene and all of the terpene compounds (i.e. matrix gas) was injected into both GC systems to check relative retention times and mass spectra, as shown in Figures 3-5a,b. These studies of standard mixtures of the hydrocarbons of interest showed that there were no significant matrix effects resulting from the simultaneous presence of the biogenic species on GC peak retention times and areas.

Two different GC oven temperature programs were used in separating and analyzing biogenic hydrocarbons. Subambient (initial temperature : 5°C) and ambient (initial temperature: 35°C) temperature programs were used for qualitative analyses, but only the latter program was used for hydrocarbon quantification during this project. The temperature programs did not appear to greatly differ in terms of terpene separation. Field samples were quantified using the Tekmar/GC/FID system. Occasionally, field samples were



Column: DB-5 (J&W)
29.5 m x 0.32 mm I.D., 1.0 μm
Carrier Gas: Helium, 20.3 cm/sec measured at 200 °C
Oven: 35°C for 2 min, 35-120°C at 4°C/min, 120-200°C at 14°C/min, 200°C for 6 min
Injector: Splitless, 100°C
Detector: ITD, 200°C
Purge & Trap: Tekmar 5010GT
Purge Time: 8 min, Helium at 20 mL/min
Desorb: 8 min at 225 °C
1. p-xylene 2. α-pinene 3. camphene 4. β-pinene 5. myrcene 6. Δ^3- carene
7. p-cymene 8. d-limonene and β-phellandrene

Figure 3-5(a). Typical Gas Chromatogram for a Standard Mixture of Terpene Compounds and p-xylene Internal Standard for the GC/ITD/Tekmar System.



Column: DB-5 (J&W)
30 m x 0.536 mm I.D., 1.5 μm
Carrier Gas: Helium, 32.5 cm/sec measured at 200 °C
Oven: 35°C for 2 min, 35-120°C at 4°C/min, 120-200°C at 14°C/min, 200°C for 6 min
Injector: Splitless, 100°C
Detector: FID, 225°C , Air Flow = 410 mL/min, H_2 Flow = 38 mL/min.
Purge & Trap: Tekmar 5010GT
Purge Time: 8 min, Helium at 20 mL/min
Desorb: 8 min at 225 °C
1. p-xylene 2. α-pinene 3. camphene 4. β-pinene 5. myrcene 6. Δ^3- carene
7. p-cymene 8. d-limonene and β-phellandrene

Figure 3-5(b). Typical Gas Chromatogram for a Standard Mixture of Terpene Compounds and p-xylene Internal Standard for the GC/FID/Tekmar System.

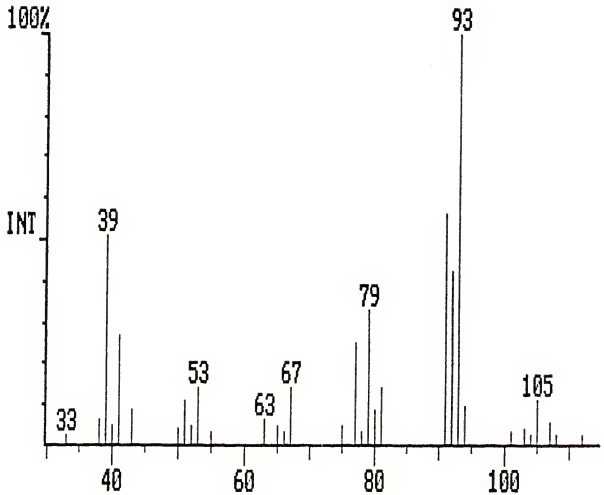
analyzed with the Tekmar/GC/ITD system to verify the terpene content from mass spectral cracking patterns and relative retention times. The precision of retention time data (% relative standard deviation, RSD, < 0.25%, n=55) for standard and field samples injected to the GC/FID system were excellent for every sample component injected to the system during the project period, as shown in Table 3-3. Identical mass spectral data and relative retention times were found between standards and field samples, as shown in Figures 3-6a,b and Table 3-4.

Development of GC calibration procedures

Several techniques for generating standard HC mixtures have been investigated for application in the production of stable monoterpene standards, as previously discussed. Most of the methods described including injection of a known quantity of liquid hydrocarbon at room temperature to a bag, dilution flask, or dynamic flow reactor leading to a large Tedlar bag, were found to be inadequate in providing a known, stable standard. Problems included incomplete recovery and poor reproducibility as a result of terpene instability and reactivity as well as inherent lack of volatility.

Table 3-3. Summary of Field Sample and Standard Retention Time for α-Pinene to Assess Precision for the GC/FID System.

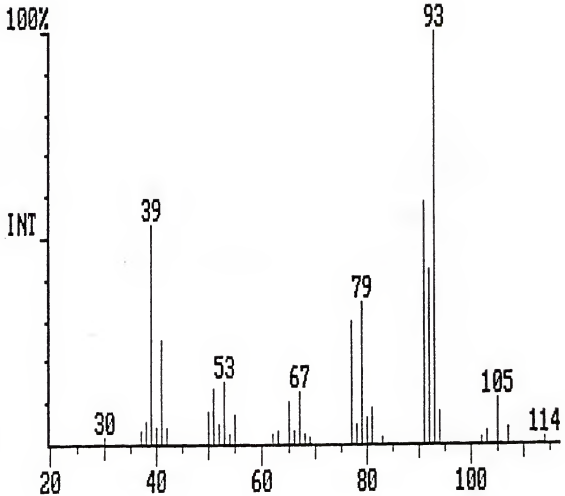
Date of Injection	Field Sample Retention Time (min)	Date of Injection	Standard Retention Time (min)
04/11/94	13.50	04/11/94	13.49
04/17/94	13.49	04/17/94	13.50
04/20/94	13.47	04/20/94	13.48
04/21/94	13.51	04/21/94	13.50
05/10/94	13.50	05/10/94	13.50
05/12/94	13.54	05/12/94	13.52
05/17/94	13.47	05/17/94	13.45
06/24/94	13.51	06/24/94	13.50
06/25/95	13.52	06/25/95	13.50
07/09/94	13.49	07/09/94	13.50
07/13/94	13.46	07/14/94	13.47
07/20/94	13.51	07/19/94	13.50
08/15/94	13.45	08/15/94	13.46
08/20/94	13.44	08/20/94	13.45
08/23/94	13.48	08/23/94	13.48
08/25/94	13.51	08/25/94	13.50
09/09/94	13.55	09/09/94	13.54
09/13/94	13.48	09/13/94	13.48
09/15/94	13.48	09/15/94	13.49
09/16/94	13.48	09/16/94	13.48
09/22/94	13.45	09/22/94	13.46
09/23/94	13.45	09/23/94	13.46
09/26/94	13.50	09/26/94	13.51
09/27/94	13.58	09/27/94	13.56
09/28/94	13.49	09/28/94	13.50
09/29/94	13.50	09/29/94	13.49
10/06/94	13.54	10/06/94	13.50
10/13/94	13.53	10/13/94	13.45
10/19/94	13.47	10/20/94	13.45
11/02/94	13.50	11/02/94	13.48
11/15/94	13.58	11/15/94	13.48
11/22/94	13.49	11/23/94	13.50
11/29/94	13.48	11/29/94	13.48
12/08/94	13.48	12/09/94	13.52
12/14/94	13.48	12/15/94	13.50
01/21/95	13.47	01/21/95	13.46
01/25/95	13.44	01/25/95	13.42
01/28/95	13.44	01/28/95	13.47
02/01/95	13.47	02/01/95	13.47
02/06/95	13.47	02/07/95	13.47
02/10/95	13.47	02/10/95	13.47
02/15/95	13.43	02/16/95	13.44
02/22/95	13.40	02/21/95	13.39
03/02/95	13.49	03/02/95	13.48
03/13/95	13.48	03/13/95	13.50
03/16/95	13.51	03/17/95	13.54
03/21/95	13.49	03/22/95	13.49
03/24/95	13.49	03/25/95	13.48
03/29/95	13.46	03/30/95	13.47
04/03/95	13.42	04/04/95	13.43
04/08/95	13.50	04/08/95	13.50
04/10/95	13.48	04/10/95	13.50
04/13/95	13.48	04/14/95	13.49
05/18/95	13.48	05/18/95	13.49
05/24/95	13.48	05/24/95	13.50
MEAN	13.49	MEAN	13.48
STD	0.034	STD	0.029
RSD(%)	0.25	RSD(%)	0.21
Number	55	Number	55



Retention Time of α-pinene: 15 min 40 sec

Mass Range: 30 to 150
Seconds/Scan 0.500 # uScans 8
Mult Voltage: 1850 volts
Transfer Temperature: 200 °C
Peak Threshhold: 1
Mass Defect: 100 mmu/100amu

Figure 3-6(a). Mass Spectral Cracking Pattern for α-Pinene from a Hydrocarbon Standard using Perkin Elmer 8420GC/ITD/Tekmar System.



Retention Time of α-pinene: 15 min 40 sec

Mass Range: 30 to 150
Seconds/Scan 0.500 # uScans 8
Mult Voltage: 1850 volts
Transfer Temperature: 200 °C
Peak Threshhold: 1
Mass Defect: 100 mmu/100amu

Figure 3-6(b). Mass Spectral Cracking Pattern for α-Pinene from a Field Sample using Perkin Elmer 8500GC/FID/Tekmar System.

Table 3-4. Comparison of Mass/Charge Ratios of Fragment Ions for a Standard and a Field Sample of α-pinene using the Perkin Elmer 8420 GC/ITD.

Standard Sample			Field Sample		
Mass	Intensity	% Base	Mass	Intensity	% Base
93	60784	100	93	38718	100
91	34232	56.3	91	22715	58.7
39	30940	50.9	39	20650	53.3
92	26113	43	92	16623	42.9
79	19968	32.9	79	13319	34.4
41	16457	27.1	77	11770	30.4
77	15360	25.3	41	9808	25.3
81	8996	14.8	53	5885	15.2
53	8777	14.4	51	5369	13.9
67	8777	14.4	67	4852	12.5
51	6802	11.2	105	4336	11.2
105	6802	11.2	65	4130	10.7

It was found that the use of one of these "less than adequate" calibration procedures could yield an error in concentration estimates as large as a factor of two.

Initially, a static dilution bottle (SDB) (#14-2080, Tekmar, Cincinnati, OH), which was sealed with a septum-containing cap, was used for making calibration standards for selected monoterpenes (α-pinene, β-pinene, and d-limonene). Individual samples of high purity monoterpenes were injected into the 2 liter glass flask at ambient temperatures and the flask was heated 65°C . It was found that the stability of monoterpenes in this small volume container was undesirable for both sets of conditions, ambient and temperature 65°C. It was found that a dark residue appeared on the inside surface of the SDB when it was heated to 65°C. When the SDB was used at room temperature, part of the injected liquid terpene remained on the interior surface, producing a thin film of non-volatile material. At room temperature, the recovery of terpene compounds was poor (< 60%). When the flask was heated to 65°C, the recovery of the selected terpene hydrocarbon was improved (from <90% to >120%), but the hydrocarbons were not stable. After testing several methods for preparing standards by conventional methods it was determined that dissolution of

terpenes in methanol might provide an appropriate starting point for the preparation of standard terpene mixtures.

The use of carefully prepared mixtures of individual monoterpene hydrocarbons and p-xylene (internal standard) dissolved in ACS reagent grade methanol (Optima grade, Fisher Scientific, Pittsburgh, PA) proved to be a reliable, stable, consistent standard. These solutions when stored in Teflon sealed glass vials in a cool and dark environment proved to have long term (≈12 months) stability. These stable standard solutions can be used for direct injection, using a syringe, to a sorbent tube or to a flowing inert gas stream for developing calibration and quality control standards. Typical recoveries of these standard mixtures were greater than 95% and reproducibilities were less than ±1% (% relative standard deviation(RSD), n=4). A typical calibration curve for a representative compound is displayed in Figure 3-7. Sensitivities (method detection limit=3 std. dev.) for GC-FID analyses were determined to be less than 0.3 ng for all of the terpenes studied.

A dynamic dilution system developed from a system recommended in EPA method 18 was used to generate gas phase calibration standards for three of the major monoterpenes

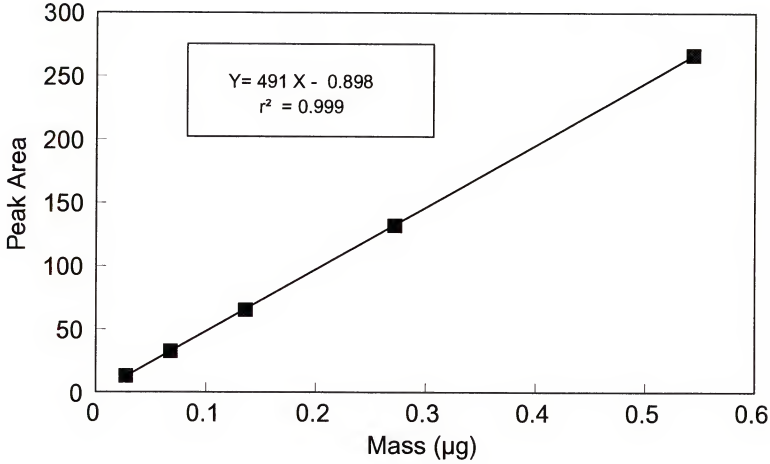


Figure 3-7. Typical Calibration Curve for α-pinene using Perkin Elmer 8500 GC/FID and Tekmar 5010 GT Systems.

(i.e., α-pinene, β-pinene, d-limonene) found in field samples and for p-xylene (an internal standard), as shown in Figure 3-8. The procedures developed to prepare gaseous monoterpene calibration standards in a large Tedlar bag (25 L) (#232-15, SKC, Pittsburgh, PA) were as follows:

1. Calculate the required mass of terpene and the required volume of carrier gas to provide the concentration required.

2. Fill an Erlenmeyer flask with water and set on a heating plate to provide a water temperature of approximately 90 degrees Celsius with moderate stirring. Place the glass trap with septum in the heated water bath.

3. Coil the heating tape at the exit of the trap to provide an exit temperature between 70 and 75 °C.

4. Start the carrier gas (pre-purified nitrogen, Bitech, Tampa, FL)) flow through activated charcoal and set the desired flow rate on the mass flow controller #251-4A, Kurz, Monterey, CA). Based on the actual mass flow rate and the desired final volume calculate the required time for carrier gas flow.

5. Attach a clean empty Tedlar bag to the exit line of the trap, open the valve on the Tedlar bag and start the timer simultaneously.

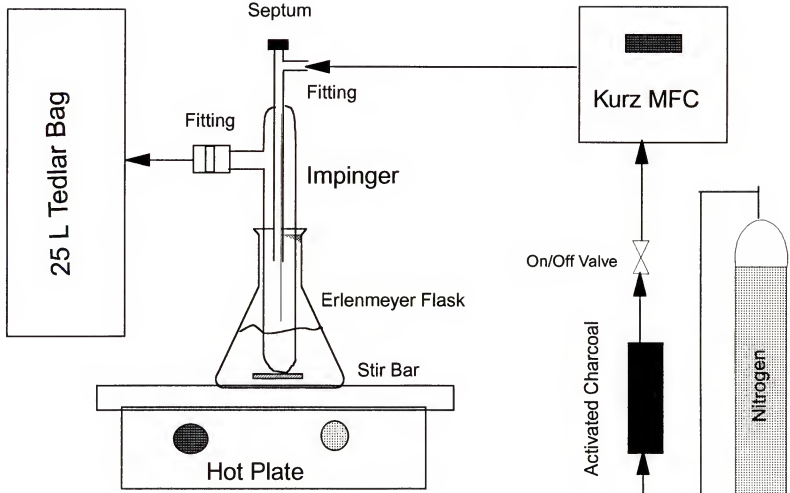


Figure 3-8. Apparatus for Dynamic Dilution System

6. Record the flow rate through the mass flow controller.

7. Inject the required volume (mass) of sample through the septum using a liquid syringe.

8. After injecting the sample snug the septum cap to prevent any leakage.

9. Observe the time, exit temperature and gas mass flow rate.

10. Stop flow of dilution gas at the calculated time by first closing the dilution gas entry valve and then the Tedlar bag valve.

11. Record the final time and air temperature.

About two hours of mixing time in a dark and cool area should be allowed before using the gas standard mixture contained in the bag. Standard gas samples were taken from the bag with a gas tight syringe and introduced to a Tenax trap sealed in the furnace section of the Tekmar automatic desorber using a helium gas flow through the trap between 0.14 and 0.15 L/min. Methanol, air and moisture were prepurged from the Tenax trap before desorbing the standard sample from the trap. The concentrations of field samples of α-pinene were found to be about two times higher than those for β-pinene and four times higher than those for d-limonene. Standard samples in the range from 0.02 ppmv to 10 ppmv of

the terpenes of interest were made and tested. Differences in the two calibration methods described above are compared in Table 3-5. Standard solutions of terpenes in methanol were injected into the SDB at room temperature to see if further improvement in recovery and stability of monoterpenes was possible. It was found that translucent films were formed inside the SDB when the dilution bottle was stored at room temperature in the dark. Only the recoveries of α-pinene and p-xylene were improved, which were 100±10% and 100±5% respectively. The recoveries of β-pinene and d-limonene were very low (35%) and high (128%), respectively. These results suggested that polymerization or isomerization of certain terpenes might occur inside the SDB, probably because the volume of the container was small (2 liters). It may be concluded, therefore, that monoterpenes must be expanded into a large volume container in order to be completely vaporized and stable in the gas phase.

Development of a Sampling Technique for Estimating Monoterpene Emissions from Vegetation (Trees)

Even though several field-tested techniques for measuring biogenic NMHC emissions from trees have been developed, many of these methods have inherent advantages and limitations.

Table 3-5. Comparison of differences in results from two calibration methods for major terpene hydrocarbons.

Run #	Percent difference (%)				
	Run 1	Run 2	Run 3	Run 4	Run 5
α-pinene	*	+4.5	+3.5	+0.3	+3.6
β-pinene	+4.9	+4.5	N/A	N/A	0.0
d-limonene	-1.5	+1.4	N/A	N/A	+3.9
p-xylene	+1.2	+3.6	N/A	N/A	+3.1

Note: "*" indicates that the peak area obtained was out of range from calibration curve.
"+" indicates methanol mixture approach has better collection of terpenes than gas phase mixture injection.
"N/A" not available

Of the sampling methods currently in use, the vegetation enclosure technique (VET) is considered to be more reliable, feasible, cost-effective, and direct than the other methods discussed in Chapter 2. Zimmerman's method, however, shows a large imprecision in emission estimates that is equivalent to about ±1 order of magnitude (Zimmerman, 1979a). The results using this method are difficult to replicate and may reflect normal variations in emission rates from different samplings of the same vegetative species (Dimitriades, 1981).

Monoterpenes and isoprene emission data obtained using Zimmermann's vegetation enclosure techniques have been compared with those derived using other techniques, such as EBBR, GEC, or AGP (Tingey et al., 1978; Zimmermann, 1979a,b; Knoerr et al., 1981; Arnts et al., 1982; Seila et al., 1982). Although the enclosure method measurements displayed higher variances than the other methods, a statistical comparison of these techniques indicated no significant difference among the results.

The vegetation enclosure sampling technique using a semi-static approach, however, has several disadvantages. One of these disadvantages is the possibility of disturbance of vegetation emission by the sample collection procedure itself

(Zimmermann, 1979a). Furthermore, the technique is not cost effective. It is likely, therefore, that the imprecision of the method could be improved by a different sampling approach.

Development of a new method has evolved from the necessity for eliminating some of the limitations and disadvantages inherent in the currently accepted VET approaches such as, Zimmermann's semi-static enclosures or dynamic flow-through chambers (Winer et al., 1983). In the current project, a vegetation enclosure chamber, that uses a Tedlar bag and external support wires, was designed and tested in the laboratory. The enclosure chamber was then evaluated in the field for suitability as a reproducible and efficient sampling environment for studying hydrocarbon emissions from a variety of plants.

The enclosure chamber was initially tested in the laboratory with ethanol vapor (≥97% purity, Fisher Scientific, Pittsburgh, PA) and subsequently it was tested with the monoterpenes of interest. Ethanol vapor was continuously injected into a constant flow of zero air through an enclosure chamber (19 L) using a vacuum pump at about 0.15 L/min in order to observe physical mixing phenomenon and approach to equilibrium of the ethanol vapor inside the Tedlar bag. About

35 minutes was found to be necessary after injection to reach equilibrium, as shown in Figure 3-9a. Also, it was found that the same time (~35 minutes) was necessary to remove all of the ethanol vapor from the enclosure bag when the ethanol injection was terminated (Figure 3-9b). Emission simulation tests with monoterpene and methanol mixtures were carried out following the initial emission simulation study with ethanol. A Model 355 syringe pump (Sage Instruments, Oregon Research Inc.) was used to generate gas phase terpenes (α-pinene, β-pinene, d-limonene) and p-xylene mixtures in zero-air flowing through the bag. The results of these simulated emission tests with ethanol are presented in Table 3-6a. The recovery of ethanol, that was continuously injected into the enclosure chamber, was about 101% (n=4) and that for total monoterpene hydrocarbons was about 109% (n=3). The results of emission simulation tests using methanol-terpene mixtures are shown in Table 3-6b.

The enclosure chamber, which has been designed for field emission rate determinations from either a whole plant or certain plant organs (e.g., branches or buds), is shown in Figure 3-10. A wooden frame (i.e., sampling box) was constructed to house all the instruments, except the zero air

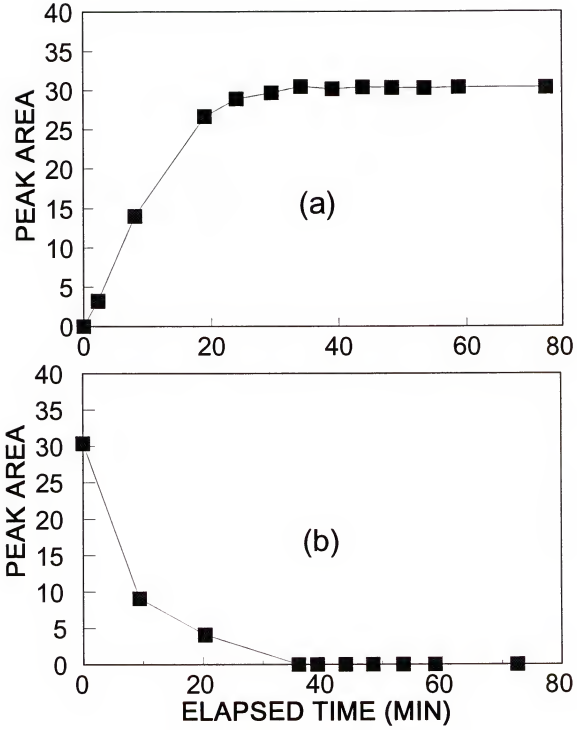


Figure 3-9. Approach to Equilibrium (a) and Flush Test (b) using Ethanol Injection into Zero Air (~0.15 L/min) and 19 L Tedlar Bag.

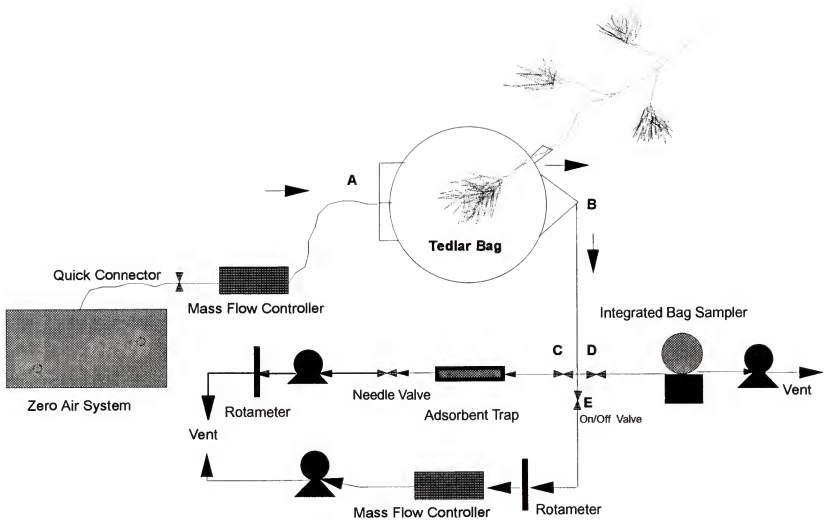


Figure 3-10. Sampling Train for Developed Emission Rate Determinations.
note: sample port 'D' is optional.

system. The zero-air generator (#111, Thermo-Environmental, Hopkinton, MA) and an air compressor (GAST#1HAB-11-M100X, MFG Corp., Benton Harbor, MI) were located in a shelter at the site and a long Teflon tube connecting the zero air generator to the vegetation enclosure chamber was used to transport zero air.

The vegetation emissions sampling method involved enclosing the branch in a Tedlar bag supported and surrounded on the outside by wire mesh. The enclosure is left open at one end and at both ends of the chamber are mounted on/off valves. At the open end of the bag, two-inch wide and half-inch long lines were drawn in the middle of the outside edge of the bag. The same markings are made on the other side of the bag, making sure that the two sets of lines match up. A tape is attached to the inside of the bag and is aligned with the lines drawn on the opposite side. The same thing is done to the other side of the bag. A 2.1 inch long piece of double sided sticky tape is taped to the inside of the enclosure bag over the lines. The same procedure is repeated for the other side of the bag. The tape is used to keep the pine branch being sampled in place and to ensure that the bag makes a good

Table 3-6a. Testing of a Modified Enclosure Technique.

Observation #	Emission Rate(ER) for Ethanol (μg/min)	Measured ER for Ethanol (μg/min)	Recovery (%)
1	387.9	382.7	98.7
2	532.9	572.1	106
3	580.2	549.0	95
4	383.9	407.2	106

Note: The flow rate of zero air was 2 liters per minute. The recovery of ethanol was 101 ± 6 %.

Table 3-6b. Testing of a Modified Enclosure Technique.

Obs #	Emission Rate for α-pinene (μg/min)	Measured ER for α-pinene (μg/min)	Recovery (%)
1	0.140	0.141	99.3
2	0.111	0.125	113
3	0.110	0.127	115

Note: The recoveries of the other hydrocarbons were very similar to that for α-pinene.

seal. Since the sticky sides of tapes were not exposed to air inside Tedlar bag, it was found that they did not cause any contamination inside the bag. Having prepared the bag for sampling, the following procedures were undertaken:

1. Leak checks of the sampling systems were conducted to make sure that the sample will not be diluted with ambient air. Background samples were taken for analysis to determine if there was contamination of the sampling system.

2. The zero-air connecting tube was quick-connected to the sampling box.

3. The main switch on the sampling box was turned on and the flow rate of 5.0 L/min, was checked to ensure that it was correct.

4. Tubes A and B on the enclosure chamber were connected to the tube providing zero-air and the tube leading to the sample outlet, which leads to the sampling box, respectively, as shown in Figure 3-10.

5. A pine branch was selected, which should be small enough so that the needles do not touch the sides of the bag when fully extended and the open bag was carefully placed around the branch.

6. A Handy-Lok closure device (Instruments for Research and Industry, I2R, Inc., Cheltenham, PA) was used to close the open end of the Tedlar bag and spring clamps were attached to the closure device. A continuous air flow (5.0 L/min) into VET bag prevented water vapor accumulation from pine needles while enclosed in the bag.

7. Zero-air was supplied to the inlet of the bag at a relatively high rate of flow, 5 liters per minute for 10 minutes. This clean air flow was used to quickly flush out the ambient air that was enclosed in the bag, in about 3 air volume exchanges.

8. The zero-air and vent flow rates were then changed from 5.0 to 2.0 liters per minute to obtain a reasonable concentrations of terpene samples from needle emissions. The branch emissions and the zero-air flow were allowed to achieve steady state at these conditions. Air inside the enclosure chamber is exhausted by a vacuum pump (Gast Model #1031-102A-351X, MFG Corp, Benton Harbor, MI), with the flow rate out of the bag set to equal the air flow in to the bag.

9. After 35 minutes of conditioning at a flow through rate of 2 liter per minute (i.e., 4 volume exchanges), part of the

sample air stream was redirected to a Tenax trap (C) and the remaining air flow (E) was vented to the atmosphere.

The hydrocarbon emission rates from the branch were estimated from the product of total flow rate through the bag and the sample hydrocarbon concentrations at steady state conditions. The emission rate estimated in appropriate units were derived as follows:

Emission Rate (ng/gdw-hr) = total flow rate (L/min) x 60 (min/hr) x sample concentration (ng/L) ÷ total dry weight of needles (gdw)

or

Emission Rate ($\mu g/m^2$-hr) = total flow rate (L/min) x 60 (min/hr) x sample concentration (μg/L) ÷ total surface area of needles (m^2)

Total dry weight and total surface area of the needles were measured as described elsewhere (Johnson, 1984). The total dry weight for slash pine needle sample was in the range from 3.5 to 13.2 μg (median = 7.5 μg) and that for loblolly pine were in the range from 2.67 to 13.1 μg (median = 6.4 μg). The total surface area for slash pine needle sample was in the range from 0.04 to 0.14 m^2 (median = 0.89 m^2) and that for the loblolly pine was in the range from 0.05 to 0.17 m^2 (median = 0.86 m^2).

Advantages in using this vegetation enclosure approach over other recently used VETs are:

1. The equipment is portable, easy to use, and cost-effective.

2. No blower, vacuum pump, or fan is used internally in the emissions chamber, therefore, this method minimizes the possibility of internal contamination or sample loss by internal mechanical component.

3. Wire mesh frames are inexpensive, flexible and easy to make. This technique could easily be adapted and applied to sampling seedlings, saplings or mature trees.

4. The sampling approach, which uses a rigidly supported enclosure, reduces the likelihood of enhanced emissions resulting from mechanical disturbance of the vegetation, i.e., due to the bag touching the needles before and during sampling.

5. Although the Tedlar bag contains ambient air initially, at the time of enclosure, there is no need to correct for the presence of ambient air nor the initial volume of the bag, because the original ambient air is almost completely displaced from the bag prior to sampling.

6. Representative sampling is possible since the bag design and dynamic flow system provide for complete physical mixing of the emissions and zero air inside the Tedlar bag.

7. A portable source of zero (clean) air (i.e., from the zero-air system) is readily available.

8. There should be little or no movement of the Tedlar bag enclosing the branch during the sampling phase due to the strong supports used.

9. The dynamic flow system can be used to moderate temperature and humidity changes in the bag.

10. Good seals (minimal ambient air leakages) are possible due to the new approach taken in sealing and unsealing the Tedlar bags.

Flows into and out of the enclosure bag were controlled by two identical mass flow controllers (Model#CRP-1A, Hastings, Hampton, VA) (see Figure 3-10). Flow through the sample tube was maintained in the range from 0.15 to 0.25 L/min by a diaphragm pump (Model #JB2N050N, Universal Electric Motor, Owosso, MI) and monitored using a calibrated rotameter (Model#6-1355, Brooks, Hatfield, PA). The mass flow controllers and rotameter were calibrated every three months under field conditions and also checked in the field regularly

to determine if any substantial changes in calibration had occurred. All the rotameters and controllers used in the laboratory and the field were calibrated against a primary standard bubble flow meter (The Gilibrator, Gilian Instrument Corporation, Wayne, NJ). Calibration curves for these rotameters (r^2>0.997) and mass flow controllers were found to be linear (r^2>0.998), precise (RED < 3%), and accurate (>99% recovery) and consistent for the duration of this project.

Approach to Sampling for Estimating Airborne Monoterpenes

Ambient air sampling for terpene hydrocarbons was initiated in April 1994, when simultaneous testing of different sampling configurations were compared. Bag collection and sorbent(Tenax-TA) trapping sampling approaches were compared. The results of this comparison study were as follows:

1. Bag sampling with and without a 2 μm Teflon filter (Savillex, Minnetonka, MN) resulted in identical concentrations of α-pinene (140 pptv) being observed.
2. Tenax trap samplers, when used with and without a 40 μm metal screen (Tekmar), resulted in estimates of 50 pptv and 180 pptv for α-pinene, respectively.

3. Tedlar bag and Tenax trap samples obtained without filters yielded concentrations of 140 pptv and 180 pptv for α-pinene, respectively.

4. Bag samples collected with a Teflon filter and a Tenax trap sampler using the metal screen in a sampling adaptor (#14-1486-200, Tekmar, Cincinnati, OH) resulted in concentration estimates of 219 pptv and 140 pptv for α-pinene, respectively. These configuration studies confirmed that Tenax sorbent sampling would be more reliable but only if the metal screen is not used for air sampling to collect monoterpenes.

Ambient air samples were collected about 20 m away from the air quality monitoring shelter and at a height of 1 m above ground. The sampling train used for collecting ambient air samples is shown in Figure 3-11. The sampling train adaptor was cleaned in the UF laboratory before use. The sampling procedures were used as follows:

1. A rechargeable personal air sampler (Model PAS-3000, Supelco) was turned on for a few minutes and allowed to warm up and achieve a stable flow rate. The sampling system should be shaded from direct sunlight to prevent the system from heating.

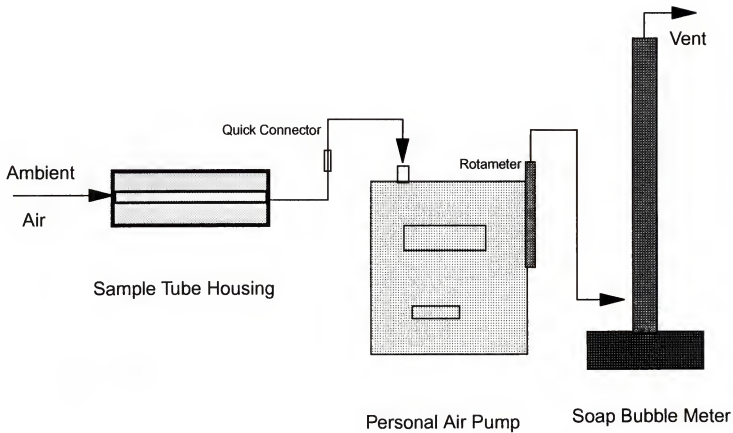


Figure 3-11. Sampling Train used for Collecting Hydrocarbons in Ambient Air at the Cary Forest Site.

2. Tygon tubing attached to the sampling adaptor containing a glass sorbent tube was connected to the personal air pump. The pump and the timer switches were turned on at the same time. The initial sampling time was recorded on a formatted sheet for ambient air sampling.

3. The flow rate of air was obtained from a soap bubble meter and recorded on the data sheet with weather condition. The sampling flow rate was checked again before completing collection of the air sample.

During these ambient air sampling excursions a known amount of p-xylene was occasionally spiked on to a clean Tenax tube during ambient air sampling exercise. This sample was stored in a clean tube container(Tekmar), and shipped to the UF laboratory with the ambient air samples for analysis. The mean and relative standard deviation recovery for spiked p-xylene samples was 98.1 and 3.2%, respectively, for six samples.

Several Tenax sample tubes were independently spiked with a mixture of several terpenes (α-pinene, β-pinene, d-limonene), p-xylene, and methanol in the laboratory and transported to the field site. One of these samples was stored in the laboratory. The Tenax sample tubes were exposed to

ambient air for a few minutes at the field site and then transported back to the laboratory. After one to 5 days of storage at room temperature in the laboratory, the recoveries for all terpene hydrocarbons were found to be within the range from 95 to 105%.

Sample breakthrough studies were made using different sampling flow rates and quantities of terpenes. Experimental laboratory results from these investigations using two sorbent tubes in series showed that using a flow rate of 0.86 L/min produced about 50% breakthrough at 38 °C with a loading of 150 ng α-pinene. From this work it was concluded that ambient air flow rates less than 0.25 L/min should be used for hot summer days (<40 °C) and flow rates less than 0.4 L/min should be used during the winter season (≤20 °C) in the south with the Tenax sorbent configuration conditions used. Also, it was confirmed that hydrocarbon samples should not be allowed to pass through an ordinary vacuum pump because of possible contamination or loss of sample due to reaction. If the appropriate sampling and storage requirements for terpene samples and standards are not met, errors in concentration estimates may amount to a factor of 10.

CHAPTER 4
RESULTS AND DISCUSSION

General Description

In the previous chapter a simple, cost-effective, and reliable sampling and analytical approach for determination of ambient biogenic hydrocarbons was described. This approach was developed in the UF Air Pollution program laboratory and tested in the field at the Cary Forest site. In this section the results obtained and their quality are described for ambient air and pine tree emissions measurements.

Because accuracy and precision of measurements define their quality, multipoint GC calibrations were performed to observe the stability of instrument response (Figure 3-7). Multipoint calibration checks for major biogenic hydrocarbon species were made every three months unless daily accuracy and precision single point calibration checks, which were continuously recorded on control charts, suggested otherwise.

No significant changes in instrument response were observed for the duration of this project.

Zero (blank) and span calibration checks using a calibration standard (#3) were run before and/or after field sample runs in order to check for species GC/FID response and retention time precision and to establish whether any impurities were present in field samples as a result of contamination. Typical accuracy and precision control charts of these calibration checks are shown in Figures 4-1 and 4-2, respectively. It is seen that recovery (accuracy) is within 100±5% and precision (RSD < 2 %) was excellent. The control charts also showed that the analytical instrument operated within control limits (± 3 std. dev.) at all times.

Hydrocarbon emission and ambient air samples were periodically collected at the Cary Forest site. The samples were, as described earlier, collected using glass sorbent tubes containing Tenax-TA and quantitatively (qualitatively) analyzed using the GC-FID (GC-ITD) analytical system.

Since biogenic terpene emissions provide a local source for the delivery of terpenes found in ambient air, terpene emission measurements from pine needles will be discussed first.

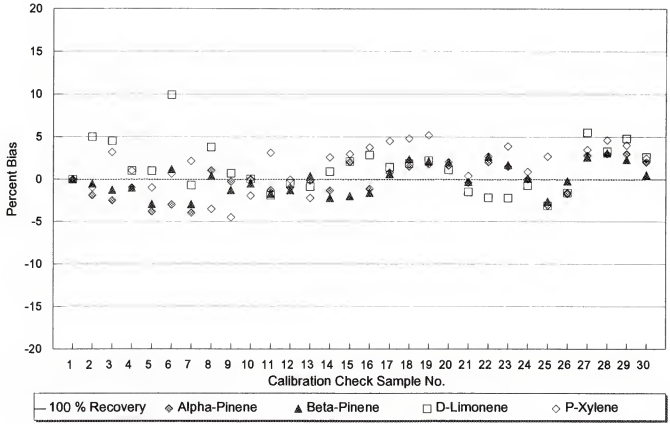


Figure 4-1. Accuracy Control Chart for Monoterpenes and P-Xylene. Calibtration Standard #3 consisted of 0.139 μg Alpha-Pinene, 0.069 μg Beta-Pinene, 0.027 μg d-Limionene and 0.028 μg P-Xylene, Syringe Injected Samples.
Note: Data shown from 6/28/94 to 6/8/95.

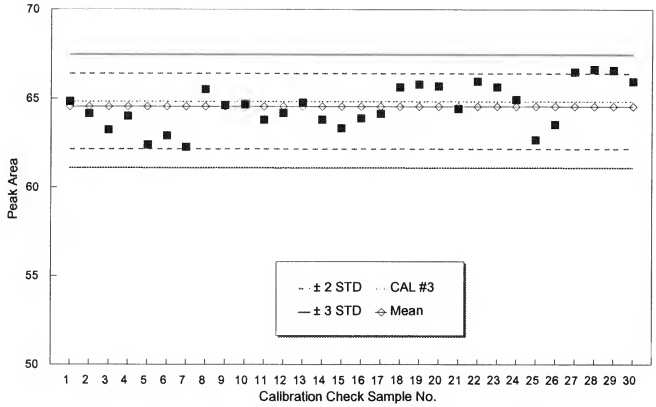


Figure 4-2. Precision Control Chart for Syringe Injected alpha-Pinene Sample (0.139 μg) Note: Data shown from 6/28/94 to 6/8/95.

Terpene Emission Measurements

Hydrocarbon emission samples were periodically collected from slash and loblolly pine saplings. These emission studies were conducted simultaneously with ambient air sampling studies at the Cary Forest site. Samples for emission rate studies were collected in glass sorbent tubes containing Tenax-TA and quantitatively (as well as qualitatively) analyzed using the GC-FID (GC-MS). Alpha-pinene, camphene, β-pinene, myrcene, d-limonene, and β-phellandrene were identified in emission samples collected from slash and loblolly pine trees. Only trace amounts of camphene, however, were found in emissions from both pine species. Trace amounts of isoprene were also found in emissions from slash pines during the summer of 1994. The unique emissions of the latter compound were studied further by Armendariz (1995).

Research groups have used different units for expressing biogenic hydrocarbon emission rates. In many of the early studies, emission rates based on unit foliage weight were used, which may be suitable for treatment comparisons, but are

not appropriate for comparing absolute rates of hydrocarbon emissions from a whole tree or organ. Needle surface area should provide a better basis for comparing emission rates since hydrocarbons are emitted from the needle surface (Johnson, 1984). Two different emission rates, one based on needle dry weight and the other on total needle surface area are presented here. Also, the emission rates reported here refer to the mass of the individual terpene hydrocarbon, not an equivalent carbon (C) emission, which has been used for biomass balance studies. The environmental temperature of the pine needles was assumed to be the needle temperature in all cases.

Seasonal Trends in Biogenic Hydrocarbon Emission Rates

It has been suggested that a relatively large tissue pool of needles and the terpene vapor pressures control hydrocarbon emission rates from pine trees (Tingey et al., 1981). Because of the influences of stomatal opening and the diffusivity of monoterpenes in the mesophyll on hydrocarbon emission rates, environmental temperatures must play a significant role in controlling the terpene emission rates from pine needles (Simon et al., 1994).

Emission samples from slash and loblolly pines were collected over a 12 month period from the summer of 1994 through the spring of 1995.

Slash Pine Emissions

Third and Fourth Quarters of 1994. Slash pine emission samples were collected during the summer (July-September) and fall (October-December) quarters. Specifically, during this period sampling was initiated on June 25, 1994 and completed on December 8, 1994. Environmental temperatures measured during the sampling period were in the range from 31.2 to 33.1 °C during the third quarter (summer) and varied from 24.5 to 32.0 °C during the fourth quarter (fall). The terpene emission rates (TERs) were found to vary considerably during these two seasons. Total TERs for slash pine saplings appeared to decrease significantly from mid-summer month to late fall, as shown in Figure 4-3. Total TERs from slash pine saplings varied from 183 to 278 $\mu g/m^2$-hr during the summer quarter (Julian days: 189 to 258) (see Table 4-1). Whereas total TERs measured during the fall quarter (Julian days:279 to 342) varied from 30 to 162 $\mu g/m^2$-hr (see Table 4-2). The maximum emission rate (278 $\mu g/m^2$-hr at 33.1 °C) observed during the six month study period, occurred in the middle of summer

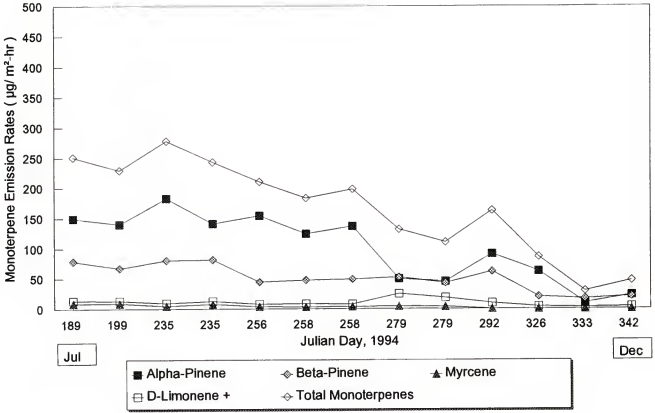


Figure 4-3. Terpene Emission Rate Trends for Slash Pine during 3rd and 4th Quarters of 1994.

Table 4-1. Statistical Analysis of Terpene Emission Rates (TERs) from Slash Pine Saplings during the 3rd Quarter (Summer) of 1994.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	147	64	6.0	11	227
STD	18	17	2.5	2.6	33
RSD (%)	13	26	41	25	14
Minimum	124	44	3.4	7.8	183
Maximum	183	81	9.0	14	278
Median	141	67	5.0	8	229
N	7	7	7	7	7

Note: The Units used for TERs above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
Detection Limit = 0.045 $\mu g/m^2$-hr.

Table 4-2. Statistical Analysis of Terpene Emission Rates (TERs) from Slash Pine Sapings during the 4th Quarter (Fall) of 1994.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	47	36	1.4	11	94
STD	29	19	2.1	9.2	51
RSD (%)	61	54	156	87	53
Minimum	9.8	17	BDL	2.8	30
Maximum	91	62	4.4	25	162
Median	48	32	3.8	6.7	98
N	6	6	6	6	6

Note: The Units used for TERs above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.09 $\mu g/m^2$-hr).

(Julian day: 235; August 23, 1994) during the two season observation period. Terpene emission rates decreased steadily commencing in the middle of September (Julian day (JD): 256) and continued until mid-December (Julian day (JD): 342), as shown in Figure 4-3. The seasonal decrease in terpene emission rates is believed to be due to a corresponding decrease in seasonal daytime average temperature as the seasons progressed. A significant singular increase in terpene emission rate observed in October (JD: 292), apparently was due to a relatively high daytime temperature (32 °C) occurring on that particular sampling day of 1994.

The emission patterns for α-pinene and β-pinene were very similar to those for total terpene emission rates observed during the sampling period. d-Limonene and β-phellandrene (d-limonene+) emissions were combined because these two unsaturated monocyclic terpenes have the same retention time for the GC-FID analytical system conditions used for quantification. However, the two isomeric terpenes (d-limonene and β-phellandrene) were easily differentiated by GC-ITD analyses. The latter system being used for the qualification of hydrocarbon constituents in emission samples. Some of the emission samples were periodically examined for

qualification of the component hydrocarbons and it was observed that the relative amounts of d-limonene and β-phellandrene were variable but that d-limonene was generally more abundant than the latter component most of the time. One sample run on August 29, 1994 showed that only d-limonene was present in emissions obtained from slash pine needles at that time.

Variations in the relative distribution of hydrocarbon emission rates for terpene samples collected and analyzed during the summer and fall, 1994 sampling periods are depicted in Figure 4-4. Alpha-pinene was found to be the most abundant compound present most of the time. Beta-pinene, also was found to be a major component of emitted terpene compounds, and, showed enhanced relative emission rates during the fall season, 1994 (see Figure 4-4). Myrcene emission rates were relatively small (< 5%) when compared to those for α- and β-pinenes. The fractional hydrocarbon emission rate (FHER) for d-limonene+ was less than 10% of the total TER, except in two cases (JD: 279) as seen in Figure 4-4. It was observed that when two samples were taken on the same day (i.e., JDs: 235, 258 and 279) and within two days (i.e., JDs: 256 and 258) similar FHERs were obtained as demonstrated by the data in

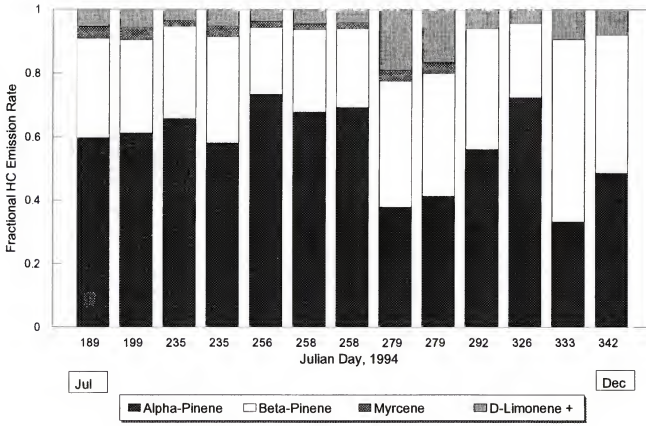


Figure 4-4. Fractional Distributions of HC Emission Rates for Slash Pine during the 3rd and 4th Quarters of 1994.

Figure 4-4. The mean FHER for α- and β-pinenes during the 3rd quarter (July-September) were 0.66 (RSD=7.7%) and 0.27 (RSD=14%), respectively (see Table 4-3). The mean fractional TERs observed during the 4th quarter of 1994 for α- and β-pinenes were 0.48 (RSD=30%) and 0.4 (RSD=27%), respectively (see Table 4-4). A decrease in the contribution of α-pinene to the overall TER was observed as a decrease in fractional hydrocarbon emission rate (FHER) as the fall season progressed.

Tingey et al. (1991) suggested that the composition of the monoterpene pool in pine species varies with season. Such changes in the monoterpene pool could lead to both qualitative and quantitative changes in individual terpene emission rates. Alpha-pinene emissions from *pinus densiflora* were observed to be lower in winter and higher in summer, but for *populus balsamifera*, monoterpene emission rates were highest in the spring and by the summer the emissions had essentially ceased (Tingey et al., 1991). Lerdau et al.(1994) studied monoterpene emissions from ponderosa pine. They found that α-pinene and β-pinene emission rates exhibited a close relationship with terpene concentrations in the tissue during the spring and fall seasons. These observations suggest that

Table 4-3. Statistical Analysis of Fractional TERs for Slash Pine during the 3rd Quarter of 1994.

	α-pinene	β-pinene	Myrcene	d-Limonene+
Mean	0.66	0.27	0.03	0.04
STD	0.05	0.04	0.01	0.01
RSD (%)	7.7	14	38	20
Minimum	0.60	0.21	0.02	0.04
Maximum	0.73	0.31	0.04	0.06
Median	0.67	0.27	0.02	0.04
N	6	6	6	6

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.

Table 4-4. Statistical Analysis of Fractional TERs for Slash Pine during the 4th Quarter of 1994.

	α-pinene	β-pinene	Myrcene	d-Limonene+
Mean	0.48	0.40	0.01	0.11
STD	0.14	0.11	0.02	0.06
RSD (%)	30	27	155	56
Minimum	0.33	0.23	< 0.003	0.04
Maximum	0.72	0.57	0.03	0.19
Median	0.45	0.39	< 0.003	0.09
N	6	6	6	6

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.

terpene concentration differences in plant tissue may influence emission variations observed among samples. Studies of the effects of tissue concentrations upon hydrocarbon (HC) emission rates could provide a basis for understanding the high variability in terpene distributions and rates that have plagued field studies of monoterpene emission rates (Lerdau et al., 1994).

First and Second Quarters of 1995. Field studies on saplings during the winter and spring seasons of 1995 were conducted from January 25, 1995 through June 14, 1995. Environmental temperatures were in the range from 9.8 to 28.5 °C during the winter months (Julian days: 25 to 88) and varied from 28 to 32.7 °C during the spring months (JDs: 100 to 165) for emissions data shown in Figure 4-5. Total terpene emission rates for slash pine saplings during the winter were in the range from 4.8 to 313 $\mu g/m^2$-hr, as shown in Table 4-5. Total hydrocarbon emission rates for slash pine trees during the spring season were in the range from 68 to 439 $\mu g/m^2$-hr (see Table 4-6).

Terpene emission rates from slash pines during the winter quarter 1995 (Figure 4-5), were considerably lower than those observed for the summer and fall 1994 (Figure 4-3). The mean

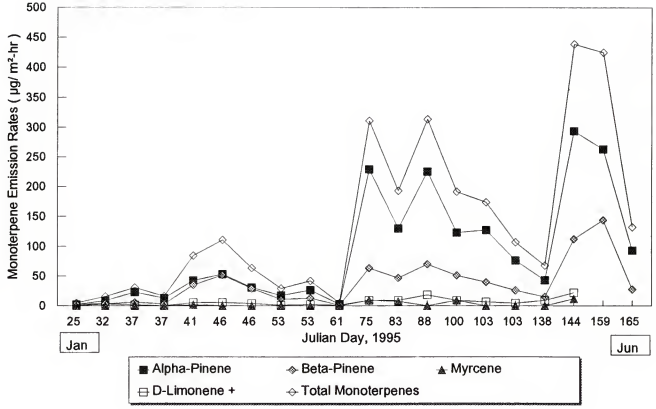


Figure 4-5. Terpene Emission Rate Trends for Slash Pine Saplings during the 1st and 2nd Quarters of 1995.

Table 4-5. Statistical Analysis of Terpene Emission Rates (TERs) from slash pine saplings during the 1st Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	62	26	1.4	4.7	94
STD	81	25	3.2	5.1	110
RSD (%)	130	97	224	109	117
Minimum	2.0	1.2	BDL	BDL	4.8
Maximum	229	70	9.6	18	313
Median	27	13	1.6	3.6	42
N	13	13	13	13	13

Note: The Units used for TER above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.07 $\mu g/m^2$-hr).

Table 4-6. Statistical Analysis of Terpene Emission Rates (TERs) from slash pine saplings during the 2nd Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	146	59	3.7	11	219
STD	95	49	5	6.6	151
RSD (%)	66	83	135	61	69
Minimum	43	15	BDL	4.6	68
Maximum	293	144	12	22	439
Median	123	40	BDL	8.9	174
NO	7	7	7	7	7

Note: The Units used for TER above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.09 $\mu g/m^2$-hr).

total TER observed during the winter was more than 10 times lower than that obtained for the summer.

In some cases unusually high emission rates were observed during the winter season quarter (JDs: 41 to 46), as shown in Figure 4-5. On these sampling days the weather conditions were very turbulent with high winds. It was observed that during sampling the VET enclosure bag moved around considerably due to the strong winds. Also, Loblolly pine samples were collected at these times, and similar emission rate increases were found for the loblolly pine trees studied under the same conditions. It was found that terpene emission rates from both slash and loblolly pines increased by more than a factor of two over those expected, during these windy days.

It was also observed during the winter season that some of the slash pine saplings produced liquid phase resins from the stems and needles. It is believed that this phenomenon occurs at a result of insect attack on the pine trees. The role of insects on terpene emissions, therefore, should not be overlooked. In addition, buds started to elongate on the branches in the middle of February, as a result of an early warm spell in north central Florida in 1995.

At the beginning of March (JD: 61) the emission rate (4.86 $\mu g/m^2$-hr) was almost the same as that (4.89 $\mu g/m^2$-hr) for January 25, 1995 (JD: 25). The similarity in these data was probably due to the low temperatures experienced on these sampling days. The environmental temperature (15.5 °C) in January (JD: 25) was very similar to that (13.6 °C) in March (JD:61).

Although the environmental temperatures were not high (i.e., 25.8 to 26.9 °C), there was a significant increase in monoterpene emission rates in the middle of March (JD : 75), which persisted through the end of March (JD : 88), as seen in Figure 4-5. The maximum emission rate for the first quarter of 1995 (313 $\mu g/m^2$-hr at 26.9 °C) observed in March was even higher than that (278 $\mu g/m^2$-hr at 33.1 °C) observed during the summer season of 1994. Also, considerable tree-to-tree variations in terpene emission rates were found for slash pines during the spring period.

In March slash pine tree buds appeared to be fully developed. This bud development is suspected to be a source for the unusually high emission rates observed in March. Two terpene emission rate measurements were conducted on a long

terminal bud at the top of a sapling in order to confirm this proposition.

Emission rates from the long terminal bud were determined based on dry weight and wet weight, as shown in Table 4-7. As expected, there was a significant difference between TERs based on wet (unit: ng/gww-hr) and dry (unit: ng/gdw-hr) weight. The terpene emission rates from developing buds are considered to make a significant contribution to the total emission rates from pine branches. The fractional distributions of HC contributions to total emissions from the terminal bud, shown in Table 4-8, were considerably different to those found in the first and second quarters of 1995, which are presented in Figure 4-6. Beta-pinene was the most abundant HC and camphene and myrcene provided less than 5% of the total hydrocarbon emission rates observed. Although β-pinene emission rates from the developed bud were higher than those for α-pinene, both emission rates were comparable. Since quantitative emission rate measurements from buds have not been studied to date, it is recommended that an effort be made to develop an approach to measuring total emission rates of terpenes. Specifically, studies of terpene emissions

Table 4-7. Terpene Emission Rates from a Slash Pine Branch with an elongating Bud.

Conditions	T = 27.6 °C		T = 28.1 °C	
Unit	ng/gww-hr	ng/gdw-hr	ng/gww-hr	ng/gdw-hr
α-pinene	72	321	68	303
β-pinene	77	341	82	365
Myrcene	2.2	9.6	5.9	26.0
d-Limonene+	9.0	40	12	52
Camphene	2.3	10	1.8	8.2
Total	162	722	170	754

Note: d-Limonene+ = d-Limonene and β-phellandrene.

Table 4-8. Fractional HC Contribution to Total Emission Rates from a Slash Pine branch with an elongating Bud.

Conditions	T = 27.6 °C	T = 28.1 °C
α-pinene	0.44	0.40
β-pinene	0.47	0.48
Myrcene	0.01	0.04
d-Limonene+	0.06	0.07
Camphene	0.01	0.011

Note: d-Limonene+ = d-Limonene and β-phellandrene.

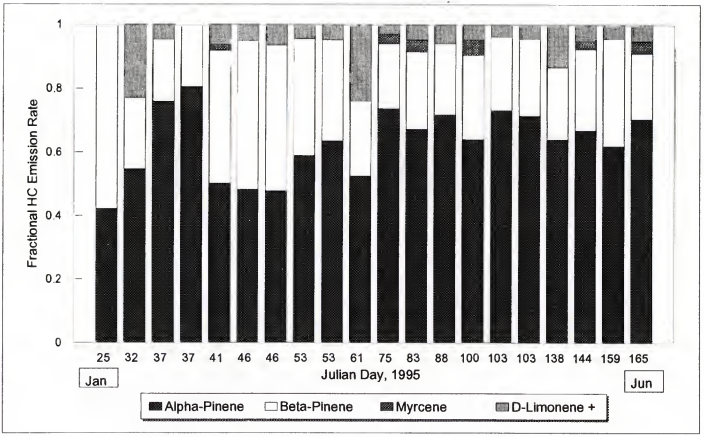


Figure 4-6. Fractional HC Distributions of Emission Rates for Slash Pine Saplings during the 1st and 2nd Quarters of 1995.

should be made from branches with new buds during this particular time in the spring.

The seasonal maximum TER for slash pines occurred during the spring period when bud elongation had actively progressed (see Figure 4-5, JDs: 144 to 159). The characteristics of slash pine stems for this specific sampling period were at the green and soft stage of development. The TERs from slash pine trees started to decrease from the middle of June (JD: 165), when the slash pine stems became almost brown and solid until the summer season commenced, as discussed earlier.

Fractional HC emission rate (FHER) distributions for individual monoterpenes observed during the first and second quarters of 1995 are shown in Figure 4-6. The FHERs of α- and β-pinenes during the first quarter (JDs: 25 to 88) were 0.61 (RSD=21%) and 0.32 (RSD=40%), respectively (see Table 4-9).

The fractional contribution of myrcene and d-limonene+ to the total emissions were 0.01 (RSD=199%), 0.04 (RSD=20%), respectively. Trace amounts of myrcene were present in slash pine emission samples most of the time during the winter sampling period.

Unusually high and low fractional HC emission rates for α-pinene occurred in January (JD: 25) and February (JDs: 41

Table 4-9. Statistical Analysis of Fractional TERs for Slash Pine Saplings during the 1st Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+
Mean	0.61	0.32	0.01	0.04
STD	0.12	0.13	0.01	0.01
RSD (%)	21	40	199	20
Minimum	0.42	0.19	< 0.005	< 0.005
Maximum	0.80	0.58	0.04	0.24
Median	0.59	0.24	0.03	0.05
N	13	13	13	13

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.

Table 4-10. Statistical Analysis of Fractional Hydrocarbon Contributions to Total TERs for Slash Pine Saplings during the 2nd Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+
Mean	0.67	0.25	0.02	0.06
STD	0.04	0.04	0.02	0.03
RSD (%)	6.4	17	130	58
Minimum	0.62	0.21	< 0.001	0.04
Maximum	0.73	0.34	0.05	0.13
Median	0.67	0.24	< 0.001	0.05
N	7	7	7	7

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.

to 46) samples, respectively, as shown in Figure 4-6. These unusual data for slash pine saplings may be attributed to the effects of strong winds and to insect attack, respectively, during the sampling periods, as discussed previously. The fractional emission rates of terpenes for slash pines observed in March, 1995 were relatively less variable than corresponding data obtained in January and February, 1995, although large variations in terpene emission rates were observed in March as discussed previously. The mean fractional HC emission rates for α- and β-pinenes during spring, 1995 were 0.67 (RSD = 6.4 %), 0.25 (RSD = 17 %), respectively, as shown in Table 4-10. Corresponding values for myrcene and d-limonene+ were 0.02 (RSD = 130 %) and 0.06 (RSD = 58 %), respectively.

Loblolly Pine Emissions

Third and Fourth Quarters of 1994. During the summer and fall quarters of 1994, samples of loblolly pine emissions were collected from June 27, 1994 (Julian day(JD): 178) through November 29, 1994 (JD: 333). Environmental daytime temperatures were in the range from 28.6 to 36.0 °C during the third quarter (summer) and varied from 28 to 29.5 °C during the fourth quarter (fall), 1994.

Hydrocarbon emission rate variations observed for loblolly pines during the summer and fall seasons are displayed in Figure 4-7. Terpene emission rates (TERs) from loblolly pines varied from 4.5 to 274 $\mu g/m^2$-hr during the summer (JDs:178 to 271) (see Table 4-11). The TERs observed during the fall of 1994 (JDs: 279 to 333) varied from 8.1 to 9.4 $\mu g/m^2$-hr as shown in Table 4-12.

In the summer of 1994 (JD:194; July 13, 1994) it was observed that the total terpene emission rate measured at 32.2 °C, drastically dropped to an extremely low level (12 $\mu g/m^2$-hr), as shown in Figure 4-7. This sample was collected about two hours after a heavy rain event. This uniquely low emission rate was a factor of 15 below expected levels. Alpha-pinene was the only measurable monoterpene in the sample. It is possible that the heavy rain event was the dominant factor contributing in this drastic decrease in emissions. This unusual terpene emission rate (TER) event suggested that further studies of the effects of needle surface wetness on terpene emission rates are needed. This conclusion will be discussed later on.

Emission rates of hydrocarbons from loblolly pines remained high until the middle of July (JD: 197), when the

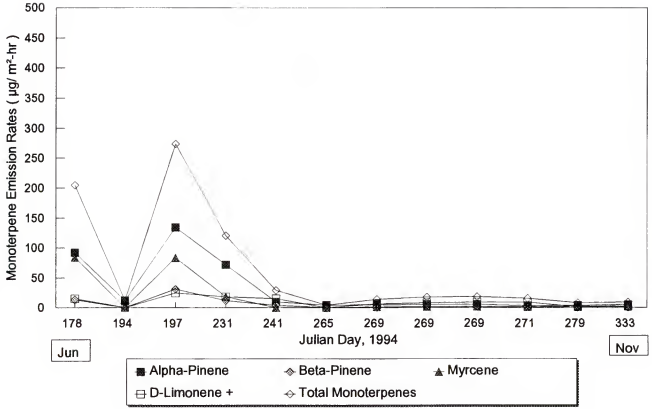


Figure 4-7. Terpene Emission Rate Trends for Loblolly Pine Saplings during the 3rd and 4th Quarters of 1994.

Table 4-11. Statistical Analysis of Terpene Emission Rates (TERs) from Loblolly Pine Saplings during the 3rd Quarter of 1994.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	37	7.4	21	12	77
STD	50	10	36	7.4	99
RSD (%)	134	137	167	61	128
Minimum	3.4	BDL	BDL	BDL	4.5
Maximum	134	31	84	25	274
Median	5.6	1.8	1.9	9.4	19
N	9	9	9	9	9

Note: The Units used for TERs above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (<0.07 $\mu g/m^2$-hr).

Table 4-12. Statistical Analysis of Terpene Emission Rates (TERs) from Loblolly pine during 4th Quarter of 1994.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	4.5	BDL	2.5	1.8	8.8
Minimum	4.1	BDL	2.3	1.7	8.1
Maximum	4.8	BDL	2.7	1.9	9.4
N	2	2	2	2	2

Note: The Units used for TER above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Sample.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (<0.09 $\mu g/m^2$-hr).

maximum TER for the summer of 1994 was observed. Emission rates decreased after the beginning of the summer season and were relatively and consistently low throughout the fourth quarter of 1994 as seen in Figure 4-7.

It was found that the fractional hydrocarbon distribution emission rates from loblolly pines varied greatly during the summer and fall of 1994 (see Figure 4-8; Tables 4-13 and 4-14). The FHERs of loblolly pines during the summer were different from those for slash pines. Examination of slash pine emissions data showed that β-pinene was the second most abundant monoterpene, whereas myrcene was observed to be the second most abundant terpene emitted from loblolly pines during the summer of 1994. D-limonene and β-phellandrene (d-limonene+) mixtures were found to be the most abundant compounds emitted from loblolly pines from August 29, 1994 (JD: 241) through September 28, 1994 (JD: 271), except for one sample obtained on September 22, 1994 (JD: 265) (see Figure 4-8).

Unusual sampling events occurred on August 18, 1994 (JD: 230) and August 19, 1994 (JD: 231). Terpene emission samples were collected from loblolly pine saplings around noon on both days. The first sample (JD: 230) was collected from a sapling

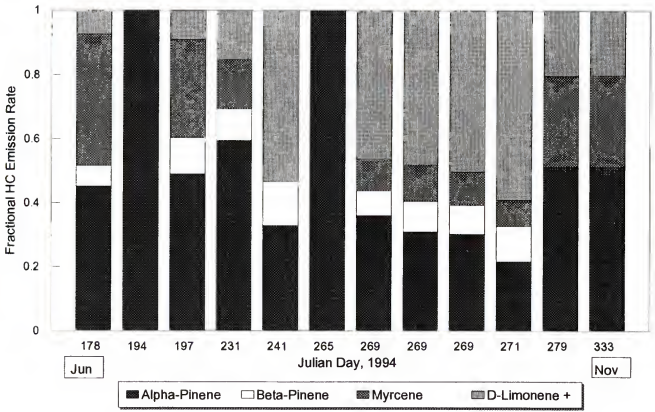


Figure 4-8. Distribution of Fractional HC Emission Rates for Loblolly Pine Saplings during the 3rd and 4th Quarters of 1994.

Table 4-13. Statistical Analysis of Fractional Hydrocarbon Contributions to TERs for Loblolly Pine during the 3rd Quarter of 1994.

	α-pinene	β-pinene	Myrcene	d-Limonene+
Mean	0.45	0.09	0.14	0.32
STD	0.24	0.04	0.14	0.23
RSD (%)	52	44	96	73
Minimum	0.22	< 0.02	< 0.02	< 0.02
Maximum	1.00	0.14	0.41	0.59
Median	0.36	0.1	0.10	0.46
N	9	9	9	9

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

Table 4-14. Statistical Analysis of Fractional Hydrocarbon Contributions to TERs for Loblolly Pine during 4th Quarter of 1994.

	α-pinene	β-pinene	Myrcene	D-limonene+
Mean	0.51	< 0.01	0.28	0.20
Minimum	0.51	< 0.01	0.28	0.20
Maximum	0.51	< 0.01	0.29	0.20
N	2	2	2	2

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

in an open field at the Cary Forest site. The sample for the following day (JD: 231) was obtained from a sapling in an open-top chamber at the same site. The open-top chamber wall was covered by plastic material and the top was also covered. Water irrigation in the open-top chamber was conducted periodically throughout the year because rain could not enter the chamber directly. Heavy rain events in June and July of 1994 included 5.1 and 8.1 inches of precipitation (UF-IFAS, 1994), respectively. Several days of major rain events occurred before collection of the first sample. Significant differences in the distributions of fractional hydrocarbon emission rates (FHERs) for the two sampling days (JDs: 230 and 231) were observed for loblolly pine emissions. Larger fractions of d-limonene and β-phellandrene mixtures (d-limonene+) were observed in the first sample of loblolly pine emissions collected in August (JD: 230). The relative abundance of d-limonene+ in the sample was much larger than that for α-pinene (this might be caused due to plant genetics). Relatively small amounts of d-limonene in the emissions mixture were observed as usual in the emission sample collected on the following day from an open-top chamber. Johnson and Allen (1994) suggests that the unusual

emissions sampling event on Julian day 230 could possibly have been due to rainfall effects.

The d-limonene and β-phellandrene mixture was the most abundant terpene emission component observed until September 28, 1994 (JD: 271), except for sampling day (JD: 265) but returned to expected values after that specific sampling time period. More studies are needed to determine the influence of precipitation (hydrology) on loblolly pine emissions in order to clarify this observation.

There were two unusual sampling events (Julian Days: 194 and 265), shown in Figure 4-8, during the 3rd and 4th quarters of 1994 when only α-pinene emissions were observed. The first event involved loblolly pine HC emission sample that was collected on July 13, 1994 (JD: 194). This sample could have been influenced by a rain event, as discussed earlier. The second sample was taken at 4 p.m. on September 22, 1994 (JD: 265). The environmental temperature during this sampling excursion was 27 °C. Also, it was recorded that a fascicle of pine needles, located outside (i.e., not inside) the Tedlar bag enclosure, was broken. On September 26, 1994 (JD: 269) at approximately 12 p.m. a loblolly pine emission rate sample was taken at the same environmental temperature (27 °C). The

emission rates for α-pinene from loblolly pines for the two different sampling days (JDs: 265 and 269), that are shown in Figure 4-7 differed by 11 percent. However, these two samples provided that the total terpene emission rates of 4.5 and 14.1 $\mu g/m^2$-hr, respectively. It is difficult to conclude why such a large discrepancy in total terpene emission rates was found at times when identical environmental temperatures existed.

Tingey et al. (1980) reported tree-to-tree variations in emission rates for slash pines at a given environmental temperature. Emission measurements were made for 14 individual slash pine trees. The individual tree emission rates at a fixed temperature were found to vary by an order of magnitude. Jutti et al. (1990), also, have found variability in α- and β-pinene emission rates for a single monterey pine tree at any given temperature varied by a factor of two. It is possible, therefore, that factors other than environmental temperature may determine terpene emission rates. In-situ replicate samples for many different sets of conditions would be required to elucidate the environmental factors affecting hydrocarbon emission rates from plants.

First and Second Quarters of 1995. The winter and spring emission rate sampling of loblolly pines was conducted from

January 21, 1995 through June 14, 1995. Environmental temperatures were in the range from 12.2 to 27.6 °C during the first quarter of 1995 (1/21/95-3/29/95). Temperatures in the second quarter (3/2/95-4/8/95) varied from 25.7 to 32.2 °C.

Terpene emission rates (TERs) in the winter season (JDs: 21 to 88) varied from 1.5 to 54.5 $\mu g/m^2$-hr and those determined in the spring season (JDs: 93 to 165) varied from 9.7 to 37.5 $\mu g/m^2$-hr, as shown in Figure 4-9 (see Tables 4-15 and 4-16). Terpene emission rates from loblolly pines observed during the winter and spring seasons of 1995 were relatively low compared to those observed during the summer and fall seasons of 1994.

Whenever terpene emission rates were found to be enhanced, as in January (JD: 28) and February (JD: 41) of 1995, there were strong winds. Wind-affected hydrocarbon emission rate enhancement phenomena and insect attack on needles were apparent for both loblolly and slash pines. Similar occurrences were observed also for slash pines, as discussed previously.

Jutti et al. (1990) used a dynamic flow-through enclosure technique, described by Winer et al. (1989), to investigate the effect of simulated wind speed. The enclosure was

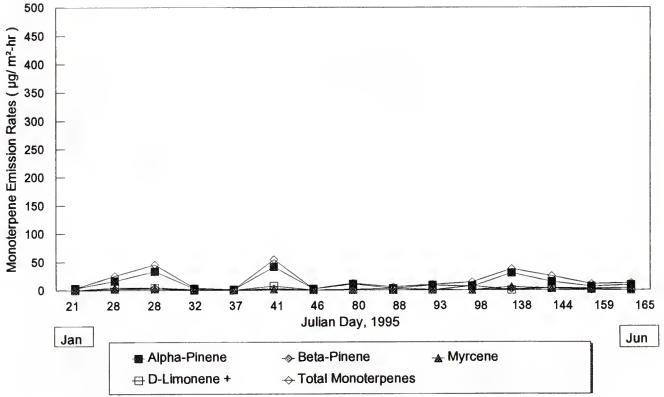


Figure 4-9. Terpene Emission Rate Trends for Loblolly Pine Saplings during the 1st and 2nd Quarters of 1995.

Table 4-15. Statistical Analysis of Terpene Emission Rates (TERs) from Loblolly Pine Saplings during the 1st Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	13	1.6	0.7	2	17
STD	15	1.8	1.1	2.9	20
RSD (%)	116	113	150	146	117
Minimum	1.5	BDL	BDL	BDL	1.5
Maximum	42	4.8	2.3	7.7	54.5
Median	3.6	1	BDL	BDL	5.8
N	9	9	9	9	9

Note: The Units used for TERs above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.06 $\mu g/m^2$-hr).

Table 4-16. Statistical Analysis of Terpene Emission Rates (TERs) from Loblolly Pine Saplings during the 2nd Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+	Total
Mean	13	1.1	1.7	2.9	18
STD	9.2	1.6	2.3	2.8	11
RSD (%)	73	147	138	97	60
Minimum	6.3	BDL	BDL	BDL	9.7
Maximum	30	4.1	5.7	7.6	37.5
Median	8.9	0.4	0.7	3.2	13
N	6	6	6	6	6

Note: The Units used for TERs above are $\mu g/m^2$-hr.
STD = Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.09 $\mu g/m^2$-hr).

equipped with a small fan. In order to study the effect of air disturbances on emissions, a household 3-speed fan was installed in the enclosure and operated at medium speed for one experiment and then at high speed for a second experiment. In addition to monoterpenes, a series of organic compounds were emitted from the fan lubrication system. This study suggests that air movement has no marked effect on monoterpene emissions from monterey pines under the simulated experimental conditions. More research is required to investigate the effect of wind on emission rates for many different species of trees since different species might provide different results.

An unusually high emission rate (160 $\mu g/m^2$-hr) for loblolly pine occurred on March 2, 1995. The enclosed branch was disturbed many times as it was difficult to set up the sampling chamber (VET). It is possible that the unexpectedly high emission rate observed might have occurred due to rough handling.

The distributions of fractional hydrocarbon composition in emission rate samples were highly variable during the 1st and 2nd quarters of 1995, as seen in Figure 4-10. Only α-pinene emissions were measurable from loblolly pine samples on

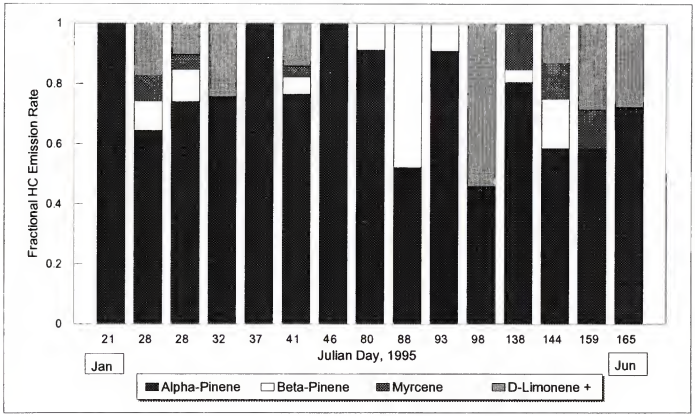


Figure 4-10. Fractional HC Composition to Total Emission Rates for Loblolly Pine Saplings during the 1st and 2nd Quarters of 1995.

January 21, (JD: 21) and February 6 and 15 (JDs: 37 and 46). Alpha-pinene is known to be the most volatile monoterpene emitted from loblolly pines, as shown in Table 4-17. Since the environmental temperatures on January 21 and February 6 (Figure 4-10) were 14.1 and 12.2 °C, respectively, observation of only α-pinene at these lower temperature conditions would be expected. However, it is difficult to explain the observation of only α-pinene appeared on February 15, 1995 because the temperature was not low (23.1 °C).

The fractional HC contributions of α-pinene, β-pinene during the 1st quarter of 1995 were 0.82, 0.09 respectively, as shown in Table 4-18. Mean fractional emission rates for α-, β-pinenes during the 2nd quarter of 1995 were 0.68, 0.05 respectively (see Table 4-19).

Seasonal Effects on Terpene Emission Rates

Seasonal variations of monoterpene emissions from slash and loblolly pines for similar environmental temperature ranges are depicted in Figures 4-11 and 4-12. Representative data sets for each month are shown in these figures. Apparently, slash pine emission rates in the spring of 1995, especially those for March, April, and May were collectively

Table 4-17. Boiling points and vapor pressures of monoterpenes.

Compounds	Boiling Point (°C)	Vapor Pressure (mm Hg)
α-pinene	156	8.8
β-pinene	164	5.9
Myrcene	167	3.4
d-limonene	178	3.3
β-phellandrene	171	2.5

Source: Tingey et al. (1980)
note: At 1 atm and 25 °C.

Table 4-18. Statistical Analysis of Fractional Hydrocarbon Contributions to TERs for Loblolly Pine Saplings during the 1st Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+
Mean	0.82	0.09	0.02	0.07
STD	0.17	0.15	0.03	0.09
RSD (%)	21	165	163	128
Minimum	0.52	< 0.005	< 0.005	< 0.005
Maximum	1.00	0.48	0.08	0.24
Median	0.76	0.06	< 0.005	< 0.005
N	9	9	9	9

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.

Table 4-19. Statistical Analysis of Fractional Hydrocarbon Contributions to TERs for Loblolly Pine Saplings during the 2nd Quarter of 1995.

	α-pinene	β-pinene	Myrcene	d-Limonene+
Mean	0.68	0.05	0.07	0.21
STD	0.17	0.07	0.07	0.21
RSD (%)	25	135	111	100
Minimum	0.46	< 0.009	< 0.009	< 0.009
Maximum	0.91	0.17	0.15	0.54
Median	0.65	0.02	0.06	0.2
N	6	6	6	6

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).
d-Limonene+ = d-Limonene and β-phellandrene.

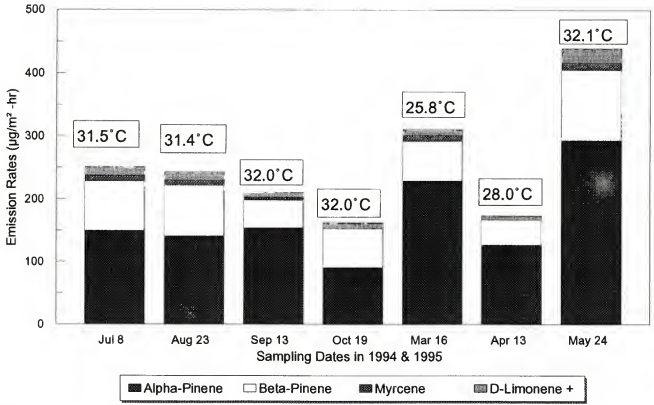


Figure 4-11. Variations in Total and Fractional HC Contributions in Slash Pine Emission Samples at Environmental Temperatures in the Range from 25.8 to 32.1 °C.

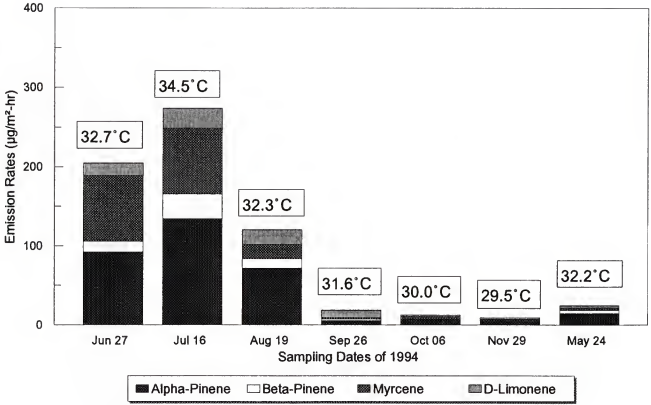


Figure 4-12. Variations in Total and Fractional HC Contributions in Loblolly Pine Emission Samples at Environmental Temperatures in the Range from 29.5 to 32.1 °C.

higher than the other seasonal emission rate values, as shown in Figure 4-11. It should be noted that environmental temperatures in March and April of 1995 were 3 to 6 °C lower than those for the summer and fall seasons of 1994. It was observed that there were noticeable changes in terpene emissions for each season (Figure 4-11). Slash pine emission rates during the spring season (1995) were unusually variable and may be attributed to bud elongation as discussed earlier.

Flyckt (1979) investigated seasonal variations in monoterpene emission from ponderosa pine trees. He reported hydrocarbons emitted from pine trees throughout the year with a significantly greater emission rate occurring in the spring. His studies of the ponderosa pine showed a maximum value of 46.9 μg/gdw-hr in the spring of 1978, decaying rapidly and maintaining a low level of approximately 2.5 μg/gdw-hr in the fall and further decreasing to 1.3 μg/gdw-hr during the winter. The average terpene emission rate in May was 18 times greater than that for the July-September period. There was no discussion, however, of bud elongation and its possible contribution to terpene emissions in the report.

Slash pine emission rates at Cary Forest in the summer and fall decreased considerably when compared to spring

emission rates for the similar range of environmental temperatures, as shown in Figure 4-11. There were no winter data available at temperatures higher than 30 °C to allow for further comparison, but the emission rates observed during the winter were the lowest presumably due to lower environmental temperatures (see Figure 4-5).

Loblolly pine emissions at similar environmental temperatures (29.5 - 34.5°C) revealed quite different seasonal patterns when compared to those for slash pine, as depicted in Figure 4-12. The highest terpene emission rates observed for terpenes from loblolly pine occurred in the summer (June-July; maximum in July) and the emissions slowly decreased in August then fell off drastically after September of 1994 and remained constant until the spring of 1995.

Temperature Effects on Pine Emissions

The importance of environmental temperature is reflected in models simulating terpene emissions. The emission rates of monoterpenes can be described by an exponential relation according to the expression:

$$Ln\ (ER) = a + b(T) \qquad (1)$$

where ER is emission rate ($\mu g/gdw\text{-}hr$ or $\mu g/m^2\text{-}hr$).

T is temperature (°C), a and b are constants dependent on the nature of the emitted terpene compound and the type of tree considered (Tingey, 1981).

As mentioned earlier, loblolly pine tree emissions are very sensitive to seasonal growth as well as to temperature variations. Application of equation (1) to observed emission rate data for this pine species showed a poor correlation coefficient (r^2=0.207,n=7) for the temperature range occurring from September to November, 1994, as shown in Figure 4-13. A further application of loblolly pine emissions data for the temperature range existing from January to March provided a slightly better correlation (r^2=0.41,n=8) between terpene emission rates and environmental temperatures.

Arnts et al. (1982) suggested that terpene emissions from loblolly pine were independent of temperature and their data showed no distinct correlation with temperature. They used a micrometeorological approach to collect samples. Zimmermann (1979b) also studied terpene emissions from mature loblolly pine trees but the data showed that in some cases emission rates decreased with temperature. A semi-dynamic VET was applied in the latter research.

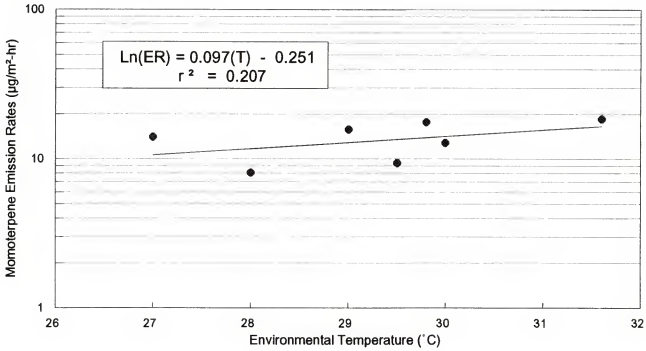


Figure 4-13. Dependence of Loblolly Pine Emission Rates on Environmental Temperature.

These earlier results suggested that loblolly pine emissions are much more variable than those observed from slash pines, as found in this work. A better curve fit for the emission rate data to equation (1) was obtained for slash pines because they appeared to less sensitive to seasonal and environmental changes than loblolly pine trees. For the temperature range from 24 to 32 °C, slash pine terpene emission rate data showed a good correlation (r^2=0.94, n=8) with environmental temperature for the period from September to early December, 1994, as shown in Figure 4-14. Also, a reasonable curve fit (r^2=0.89, n=4) to equation (1) was separately obtained for the summer months (July-August) where the latter emission rates were much higher than those obtained for the fall.

Slash pine emission rates in winter appeared to vary possibly due to the occurrence of strong winds. Consequently, data obtained during those windy days (n=3) were excluded from the curve fit to equation (1). The results are shown in Figure 4-15. A good line fit (r^2=0.95, n=5) was possible as a result of the selective exclusion of high wind data. The three data points corresponding to windy days were, then,

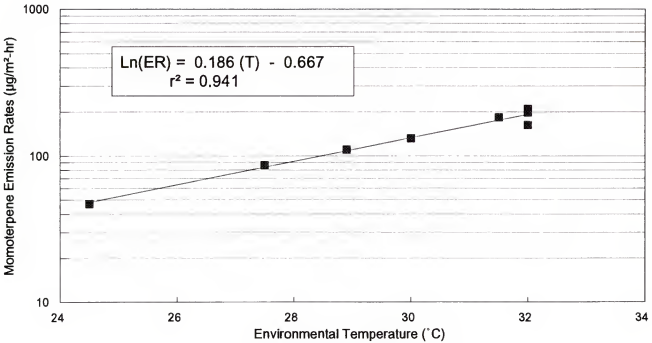


Figure 4-14. Dependence of Slash Pine Emission Rates on Environmental Temperature for September through December, 1994.

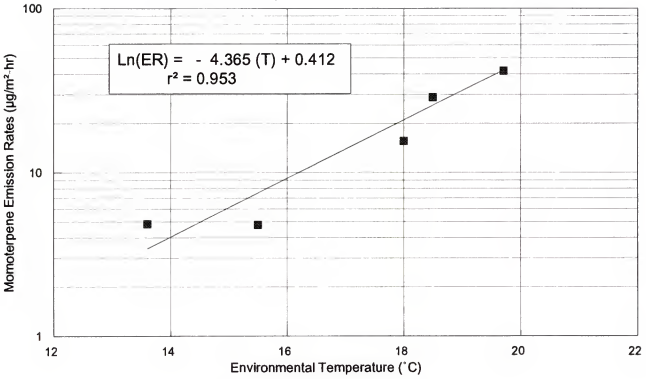


Figure 4-15. Dependence of Slash Pine Emission Rates on Environmental Temperature in February of 1995.

separately applied to the equation (1) and a high correlation resulted (r^2=0.99).

An unusual curve fit was observed for slash pine emissions data obtained during the spring (March 16 - April 10) of 1995, as shown in Figure 4-16. A weak, slightly negative correlation (r^2=0.41, n=6) between temperature and slash pine HC emissions was found. This unusual correlation might result from specific terpene emissions associated with maturing buds on the slash pine branches during spring, as discussed earlier. The emission rate data described earlier were based on total terpene emissions per unit needle surface area, however, bud emission rates were not taken into account in the former analysis.

When only α-pinene emissions from slash pines were correlated with temperature using equation (1) for the summer (July-August) and fall (September-December) seasons, 1994 determination coefficients of 0.89 (n=4) and 0.75 (n=8), respectively, were obtained.

Reproducibility Tests for Biogenic Source Enclosure System

Precision checks of the modified enclosure system used for sample collection were conducted from winter (1/25/95)

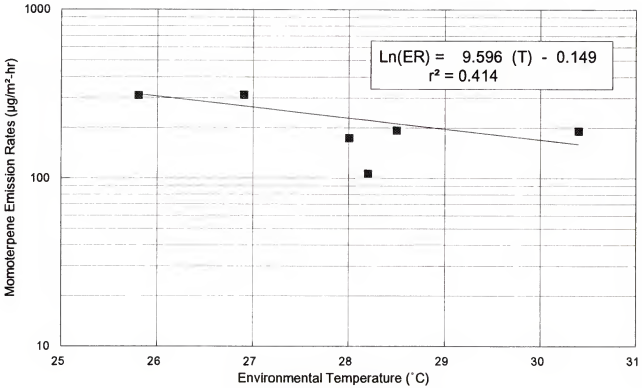


Figure 4-16. Dependence of Slash Pine Emission Rates on Environmental Temperature during March and April of 1995.

through spring (4/13/95) of 1995. These tests were applied to slash and loblolly pines when environmental temperatures were reasonably constant (i.e., within ±1 °C) during the sampling periods. Two consecutive samples (i.e., not simultaneous samples) were collected each sampling day from the two pine species during the test period.

These precision test results are shown in Tables 4-20 and 4-21. If the emission rates are constant, then the terpene concentrations in the enclosure bag should, also, be consistent after a 35 minutes exposure period to allow for equilibrium, as described in Chapter 3. Slash pine studies showed that the absolute % differences between first and second samples varied from 0.33 to 29% (see Table 4-20). The maximum difference, 29%, might have occurred due to active bud emissions during spring.

The percent differences between consecutive emission samples for loblolly pines varied from 0.74 to 24.2%, as seen in Table 4-21. Weather conditions existing when maximum bias (24%) was observed between the paired samples were not normal. Approximately three hours before setting up the enclosure system, on this particular day there was a rain event.

Table 4-20. Reproducibility of Slash Pine Emission Measurements.

Date (Time)	Temperature (°C)	Total ER ($\mu g/m^2$-hr)	% difference
Jan 25 (2 pm)	15.5	4.79	-16
Jan 25 (2 pm)	15.8	4.03	
Feb 10 (3 pm)	22.4	84.0	+4.4
Feb 10 (3 pm)	21.7	87.7	
Feb 22 (Noon)	18.5	29.0	-14
Feb 22 (1 pm)	19.0	24.9	
Mar 16 (Noon)	25.8	310.8	+29
Mar 16 (Noon)	26.7	401.0	
Mar 24 (Noon)	28.5	193.1	+0.3
Mar 24 (Noon)	29.1	193.7	
Apr 13 (Noon)	28.0	173.6	-11
Apr 13 (Noon)	29.0	155.1	

Note: % difference based on first emission data set.
Sampling time, 2 pm means between 1 pm and 2 pm.

Table 4-21. Reproducibility of Loblolly Pine Emission Measurements.

Date (Time)	Temperature (°C)	Total ER ($\mu g/m^2$-hr)	% difference
Jan 21 (4 pm)	14.1	3.62	-13.5
Jan 21 (5 pm)	14.4	3.13	
Feb 01 (1 pm)	16.3	4.07	-0.74
Feb 01 (2 pm)	16.9	4.04	
Feb 06 (2 pm)	12.2	1.47	-11.6
Feb 06 (3 pm)	12.3	1.30	
Feb 15 (1 pm)	23.1	2.60	-19.2
Feb 15 (2 pm)	23.3	2.10	
Mar 21 (1 pm)	27.6	11.77	-3.57
Mar 21 (2 pm)	27.2	11.35	
Mar 29 (1 pm)	25.9	5.78	-24.2
Mar 29 (1 pm)	26.4	7.18	

Note: % difference based on first emission data set.
Sampling time, 2 pm means between 1 pm and 2 pm.

This particular case where a rain event occurred in the middle of summer has been discussed previously and deserves further investigation of the effects of rain on emission rates from both species of pine trees.

Rough Handling Effects on Pine Tree Emissions

Several different types of rough handling may be defined as follows. Rough handling can be divided into two major groups, artificial and natural rough handling. Artificial rough handling could occur by touching, grabbing, shaking, or braking needles. Natural rough handling could be caused by wind, insect attack, or a lightning strike. More specific definitions should be developed for more in-depth studies of rough handling effects on hydrocarbon emissions sampling.

Jutti et al. (1990) carried out four experiments in which an enclosed Monterey pine tree was rough-handled prior to sampling. Rough handling was achieved by manually compressing and releasing a flexible container enclosing the tree. Pine needles were repeatedly in contact with the Teflon bag enclosure, although there was no obvious damage. The principal monoterpene levels emitted in this set of rough-handling experiments were found to be 10-50 times higher than those

produced in normal experiments, when conducted at the same temperature, but where rough handling was minimized.

Loblolly pines showed very high emission rates when the needles were grabbed prior to sampling in June and July, 1994 at Cary Forest, FL. The monoterpene emissions for this set of treatment experiments were 5 to 20 times higher than those produced in under normal conditions conducted at the same environmental temperature.

Vaporization of monoterpenes is strongly dependent on temperature. In the summer months emission rates are expected to be very high as discussed earlier. It is believed that undisturbed pine needles have very small droplets of monoterpene resin on the needle surface. Any surface contact may spread these droplets over the needle surface allowing the monoterpenes to vaporize more quickly. Terpene odors and needle stickiness have been observed to be greater in summer than for the other seasons.

At the end of fall, 1994, an experiment was conducted to test the effect of grabbing needles on a loblolly pine during sampling for terpene emission estimates. No observable difference in the emission rates of terpenes was found. In contrast, similar experiments conducted in the summer resulted

in 5 to 20 times greater hydrocarbon emission rates than normal. The results of these rough handling studies (i.e., grabbing) on terpene emission rates indicate that rough handling effects are important when emission rates are high in summer and are minimal when emission rates are low in winter.

A rough handling incident involving loblolly pine needles occurred during sampling on January 16, 1995. The terpene emission rates increased by more than an order of magnitude over normal rates after a few fascicles and needles were broken. In the beginning of the spring (March 2, 1995) sampling period another event occurred while setting up the enclosure bag around a loblolly pine branch. The branch was shaken a few times, but the needles were not grabbed. Monoterpene emission rates were 20 times higher than that expected for the same environmental temperature.

Days where average wind velocities greater than 2.5 meter per second occurred frequently during sampling periods primarily between the end of winter and early spring. Slash and loblolly pine emission rates were unusually high during these days of high winds when compared to days of lesser average wind velocities. The emission rates from slash pine trees on those windy days were found to be 3 to 6 times

greater than these for days with normal wind conditions. Similarly, loblolly pine emission rates increased by a factors from 7 to 13 on these windy days. However, the cause of these increased terpene emission rates (TERs) is not clear. Because strong wind affects the entire tree, terpene emission variations could be a result of functional variations of the pine tree. However, TER increases could be simply due to the wind physically causing rough handling. More studies of the mechanism whereby wind affects terpene emission rates must be undertaken to completely understand this process.

Needle Surface Wetness Effects on Pine Tree Emissions

Terpene emission samples were collected from wet loblolly pine needles in the middle of July (1994) about two hours after a rain event. The emission rate was found to be reduced by a factor of 15 times below normal and only α-pinene was measurable.

Lamb et al. (1984) reported that α-pinene emissions (primarily from *Pseudotsuga menziesii*) from wetted surfaces (rain or dew) were approximately an order of magnitude larger than from dry branches at a given temperature. It appears that various species respond to environmental changes in

different ways. Clearly, more study is needed to understand the effects of surface wetness on terpene emission rates from different types of vegetation.

Before discussing needle surface wetness effects on TERs, it is necessary to compare environmental temperatures with enclosure bag temperatures. This comparison was carried out using calibrated thermometers during the summer of 1994 and the winter of 1995. The bias between the two temperatures was within ±1 °C as shown in Table 4-22.

Needle Surface Wetness Effect on Slash Emissions

Two complete sets of studies were performed for slash pine saplings. Duplicate samples were collected before and after water treatment and when the needle surface was apparently dry. The duplicate samples were not collected simultaneously but consecutively, as discussed earlier. The first study was performed on March 16, 1995. The results are shown in Table 4-23. Deionized (DI) water was sprayed on slash pine needles ten times using a polyethylene spray bottle. The first sample was collected approximately 40 minutes after the water treatment. There was a significant drop in emissions by a factor of two. The enclosure bag was then opened again and exposed to the ambient environment for

Table 4-22. Comparison between Environmental and Enclosure Bag Temperature (T).

Environmental T (T_e; °C)	Bag T (T_b; °C)	T_b-T_e (°C)
14.0	14.2	0.2
14.9	14.9	0.0
25	24	-1
26.8	27.4	0.6
27	26	1
27.5	28.3	0.8
27.5	27.0	-0.5
29.5	30.1	0.6
31	31.7	0.7
31.4	31.7	0.3
32	32.5	0.5

Table 4-23. Needle wetness study #1 of Slash Pine Terpene Emission Rates ($\mu g/m^2$-hr).

Compounds	Before Treatment		After Treatment		After Drying	
	25.8°C	26.7°C	27.4°C	26.6°C	25.5°C	25.9°C
α-pinene	229.1	296.7	103.6	96.7	31.9	63.1
β-pinene	63.1	83.7	28.0	27.4	9.59	17.7
Myrcene	9.56	BDL	BDL	BDL	BDL	BDL
d-Limonene+	8.98	20.7	6.32	6.06	BDL	4.47
Total	310.8	401.1	137.9	130.1	41.5	85.3

Note: d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.07 $\mu g/m^2$-hr).

one hour. Following this exposure the emission rate decreased further to a factor of seven below normal. In fact, there was a preceding water treatment study conducted on March 13, 1995. The same branch used on March 16, 1995 was sprayed with DI water, but only after treatment data were available from this study.

The environmental temperatures for the two different days were 26.5 °C and 27.4 °C, respectively, as shown in Table 4-24. Less than 5 percent difference in terpene emission rates was found between the two water treatment studies for the same branch of a slash pine tree. These results indicated that TERs are substantially reduced after rain events and that there was good reproducibility of results obtained using the vegetation enclosure technique developed for the field work reported here.

Another rain simulation study was performed on May 24, 1995, as shown in Table 4-25. A two-liter spherical glass bottle containing DI water was used as a humidifier in this experiment. The humidifier was installed in the zero-air flow stream, prior to entering the Tedlar bag. DI water was sprayed four times on slash pine needles with a polyethylene spray bottle before enclosing the bag around the branch.

Table 4-24. Comparison of Consecutive Daily Samples of Slash Pine Emission Rates ($\mu g/m^2$-hr).

Compounds	After Treatment at 26.5 °C (3/13/95)	After Treatment at 27.4 °C (3/16/95)
α-pinene	104.1	103.6
β-pinene	30.2	28.0
Myrcene	3.71	BDL
d-Limonene+	6.6	6.32
Total	144.7	137.9

Note: d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.07 $\mu g/m^2$-hr).

Table 4-25. Needle Wetness study #2 of Slash Pine Terpene Emissions ($\mu g/m^2$-hr).

Compounds	Before Treatment		After Treatment		After Drying	
	28.5 °C	29.1°C	30.6°C	30.7°C	30.3°C	30.3°C
α-pinene	129.9	135.3	55.1	53.4	26.4	22.9
β-pinene	46.8	44.1	69.7	30.4	15.6	16.8
Myrcene	7.33	6.02	BDL	BDL	BDL	BDL
d-Limonene+	9.10	8.24	6.19	4.94	3.02	3.48
Total	193.1	193.7	131	88.7	45.1	43.1

Note: d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.07 $\mu g/m^2$-hr).

After two emission rate samples were collected, the humidifier was, quickly, disconnected from the zero-air line. Approximately ten minutes after disconnecting the humidifier, two additional emission samples were obtained sequentially. This study also indicated a significant needle surface wetness effect, causing a factor of four decrease in slash pine emission rates, as shown in Table 4-25.

Needle Wetness Effect on Loblolly Pine Emissions

Two complete sets of studies were carried out to assess the needle surface wetness effect on loblolly pine emissions. During these studies, temperatures inside and outside the enclosure bag were occasionally compared. Inside and outside enclosure-bag temperatures differed by no more than 1°C. Relative humidity, after DI water treatment, was observed to be over 70% during these treatment studies. As with slash pine, a two-liter glass bottle was used as a controlled humidity source in these studies.

The first study was conducted on March 21, 1995. The results are shown in Table 4-26. Loblolly pine trees were observed to respond to water treatment more slowly than slash pines. The results of this study indicated that loblolly pine

Table 4-26. Needle Wetness Study #1 of Loblolly Pine Terpene Emission Rates ($\mu g/m^2$-hr).

Compounds	Before Treatment		After Treatment		After Drying	
	27.6°C	27.2°C	27.0°C	26.9°C	25.5°C	24.8°C
α-pinene	10.7	10.2	13.2	11.97	7.75	5.33
β-pinene	1.04	1.11	1.09	0.99	0.84	BDL
Myrcene	BDL	BDL	BDL	BDL	BDL	BDL
d-Limonene+	BDL	BDL	BDL	BDL	BDL	BDL
Total	11.8	11.4	14.3	11.96	8.59	5.33

Note: d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.06 $\mu g/m^2$-hr).

TERs decreased by approximately a factor of two between the "Before Treatment" and "After Treatment" samples.

Another experimental field study on the effect of surface wetness (Table 4-27) was performed on April 8, 1995. In this study, the enclosure bag was not disconnected after water treatment, although the humidifier was disconnected after treatment. Two hours after the humidifier was disconnected, two samples (After Drying) were collected in sequence. It appeared that there was a significant increase in terpene emissions. This increase might have been due to rough handling, however, since the enclosure bag was opened and closed when the water spray was applied to simulate a rain event. Hydrocarbon emission rates dropped continuously by a factor of two, as seen previously from the data in Table 4-27. It is possible that the high sensitivity of loblolly pine to rough handling may have been counteracted by a corresponding emission rate decrease due to needle surface wetness.

Clearly, more studies are required under different conditions to determine the dominant emission rate factors under complex conditions.

Table 4-27. Needle Wetness Study #2 of Loblolly Pine Terpene Emission Rates ($\mu g/m^2$-hr).

Compounds	Before Treatment		After Treatment		After Drying
	26.4°C	26.3°C	27.5°C	27.6°C	24.7°C
α-pinene	6.42	7.94	12.6	9.79	3.25
β-pinene	BDL	BDL	BDL	BDL	BDL
Myrcene	BDL	BDL	BDL	BDL	BDL
d-Limonene+	7.59	8.79	20.9	10.8	3.77
Total	14.0	16.7	33.4	20.6	7.02

Note: d-Limonene+ = d-Limonene and β-phellandrene.
BDL = Below Detection Limit (< 0.06 $\mu g/m^2$-hr).

Emission Rate Comparison

The emission rates obtained from slash and loblolly pine saplings during the summer of 1994 were compared with data reported by other workers. For data comparison purposes, a common unit based on dry weight is used as most of the previous work was reported using this unit. Various research groups have used different sampling and analysis approaches, therefore, this comparison was based solely on the assumption that temperature alone controls the emission rates of HCs emitted from pine trees.

Current slash pine emissions data obtained at 30 °C were compared with data from previous work. Current work, reports by Zimmerman (1979b), and Tingey (1981) provide mean total monoterpene emission rates of 3.2, 2.9, and 7.2 μg/gdw-hr at 30 °C, respectively. The difference between Zimmerman's data and current data is only ten percent. However, the data obtained from Tingey was approximately two times higher than the current data. Zimmermann (1979b) took samples from mature slash pine trees at a field site. Current data was obtained from pine saplings at the Cary Forest site. Tingey studied 15 month old seedling samples using a laboratory gas exchange

chamber. Johnson and Allen (1994) have described age effects on emissions of monoterpenes. Such effects may explain the differences in the data reported and the techniques applied by other research groups. However, other factors such as time of year, types of soil, different geographical locations, soil fertility (Johnson and Allen, 1994) can play important roles in determining terpene emission rates.

A comparison of current loblolly pine emissions with those from Arnts et al. (1978) yields mean emissions estimates of 1.5 and 4.2 μg α-pinene/gdw-hr at 30 °C, respectively. The difference between Arnts' group (meteorological approach) and the current study (VET method) was approximately a factor of 3. Arnts' group suggested that TERs were independent of temperature and their data showed no distinct correlation with temperature. Zimmerman (1979b) also studied TER samples from mature loblolly pine trees but his data showed that in some cases the TERs decreased with increasing temperature. These results suggest that loblolly emissions are much more variable than those from slash pine, as found in this work.

Ambient Air Measurements

Ambient air samples were collected at the Cary Forest site about 1 m above the ground. These samples were qualitatively analyzed initially using GC/ITD techniques. Although α-pinene, β-pinene, d-limonene, β-phellandrene and p-cymene, were found from emission studies of slash and loblolly pine trees, the latter two compounds occurred in ambient air samples at levels below the analytical method detection limit (~ 2 pptv, based on a 20 L air sample) most of the time. Only α-pinene and β-pinene were found to be consistently abundant in the forest air. Isoprene (C_5H_8), a highly reactive natural diene, was also found in ambient air samples. This singularly reactive compound has been quantified in a preliminary study by Armendariz (1995).

Arnts and Meeks (1981) have summarized other work on the determination of ambient biogenic hydrocarbon concentrations, which was carried out from 1965 to 1980. They suggested that surrounding vegetation (i.e., local sources of hydrocarbons) contributes substantially to ambient biogenic hydrocarbon levels. For example, in a forest of oaks and other hardwoods,

only isoprene was found to be present as the predominant hydrocarbon compound, since these trees are the principal emitters of isoprene.

Seasonal Trends in Ambient Monoterpene Concentrations

In the current field studies there were large variations in ambient monoterpene levels characteristic of seasonal emission changes. Ambient air measurements were conducted periodically during the observation period from April 8, 1994 through June 14, 1995.

Ambient concentrations of total monoterpene hydrocarbons reported in the literature range from <10 pptv to 18 ppbv, depending upon local meteorology, type of and distance from biogenic emission sources (Arnts and Meeks, 1981; Riba et al., 1987; Peterson, 1988).

Second Quarter (Spring) of 1994

Air sample collection for estimating ambient terpene concentrations was initiated in the spring of 1994. This initial study was carried out from April 8, 1994 through June 25, 1994. Ambient terpene levels during this season were observed to vary considerably from month to month, as shown in Figure 4-17. The total monoterpene concentrations were in the

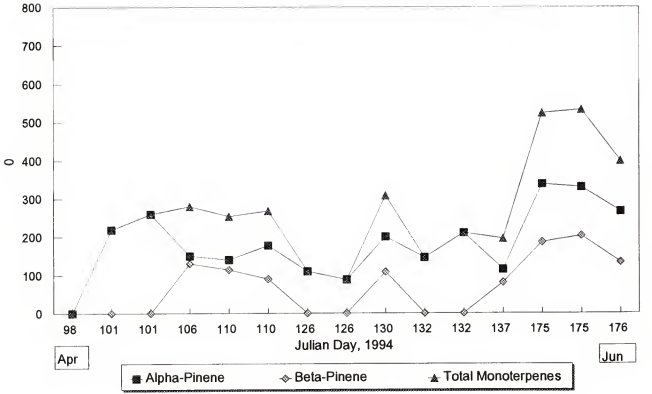


Figure 4-17. Seasonal Ambient Terpene Concentration Trends during the 2nd Quarter of 1994.

range from 88 to 533 pptv. The first sample (JD: 98), shown in Figure 4-17, was measured at 3 m above ground on a windy day. These meteorological conditions have generally been the reason that ambient levels were below method detection limit (~2 pptv based on 20 L sample). This datum, therefore, was excluded from data comparisons, as a result of these unusual conditions.

The mean total terpene concentration found for the spring quarter (April through June, 1994) was 271 pptv (RSD =50 %). Also, the mean ambient terpene concentration level for June, 485 pptv (RSD = 15 %), was substantially greater than those for April, 256 pptv (RSD = 9 %), and for May, 176 pptv (RSD = 45 %). a statistical analysis of spring quarter 1994 is shown in Table 4-28. Holdren et al. (1979) measured ambient monoterpene concentrations in a rural coniferous forest area (pine, fir) in the Northwestern U.S. from July through September, 1976; November, 1976 and April, 1977. Alpha-pinene, β-pinene, Δ^3-carene, and d-limonene were measured in the latter study. Monoterpene levels were reported to be in the range from <40 pptv to 1.55 ppbv at 1 meter above ground but less than 40 pptv outside the forested area. The average total monoterpene concentration reported by Holdren et al.

Table 4-28. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 2nd Quarter (Spring) of 1994.

	April	May	June	Quarter
Mean	256	176	485	271
STD	23	80	75	135
RSD (%)	9	45	15	50
Minimum	219	88	399	88
Maximum	280	308	533	533
Median	260	171	524	257
N	5	6	3	14

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

Table 4-29. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 2nd Quarter (Spring) of 1994.

	α-pinene	β-pinene
Mean	0.78	0.22
STD	0.2	0.2
RSD (%)	26	92
Minimum	0.54	< 0.006
Maximum	1	0.46
Median	0.67	0.33
N	14	14

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

(1979) was 273 pptv for the monitoring period. The average concentration found for forest floor samples was 414 pptv. Average terpene concentrations reported for the month of April was the lowest during the whole sampling period at 61.6 pptv (RSD =7.6 %) for n=3.

In May of 1976 a three-day ambient air sampling study was conducted in the St. Petersburg/Tampa, Everglades, and Miami, Florida areas to assess the importance of naturally emitted hydrocarbons in ozone production (Lonneman et al, 1978). Monoterpene concentrations were found to be below the method detection limit (100 pptv). It should be noted, however, that this method detection limit was about 50 times higher than that obtained in the current research project.

Fractional ambient concentrations of α-pinene and β-pinene during the spring quarter at the Cary Forest site varied considerably on a monthly basis, as can be seen in Figure 4-18. The average total terpene weight (mole) ratio for α-pinene (0.78) was much greater (3.5:1) than that for β-pinene (0.22) (see Table 4-29). This result indicated that α-pinene was the predominant terpene compound present in ambient air during the sampling period.

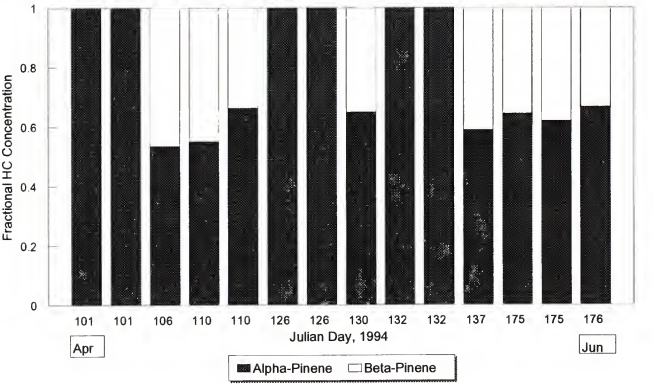


Figure 4-18. Fractional Distributions of Ambient Hydrocarbon Observed during the 2nd Quarter of 1994.

Third Quarter (Summer) of 1994

Ambient air sampling in summer was performed from July 8, 1994 through September 26, 1994. The first sample of the season, (JD: 189), shown in Figure 4-19, was measured near a terpene emission source (about 2 m away). The next three samples collected showed that ambient terpene levels were relatively low even though ambient air temperatures were higher than normal (i.e., 36.7, 38.0 and 29.0 °C, respectively). The low levels of terpene observed for the latter samples may have occurred due to frequent rain events and intense sunlight observed in July and August. The low terpene concentrations reported here for early summer, however, were similar to those found in other coniferous forests, notably by Seila et al., (1983), Riba et al., (1987), Yokouchi and Ambe (1988) and Johansson and Jason (1993).

An unusually high level (930 pptv) of total monoterpene occurred at the Cary Forest site at the end of August, 1994. This unusual value was excluded from statistical data analysis for the summer season to avoid distortion of the general tendency of the ambient terpene concentrations. The mean total terpene concentration estimated for September, 380 pptv (RSD = 14 %), however, was much greater than corresponding

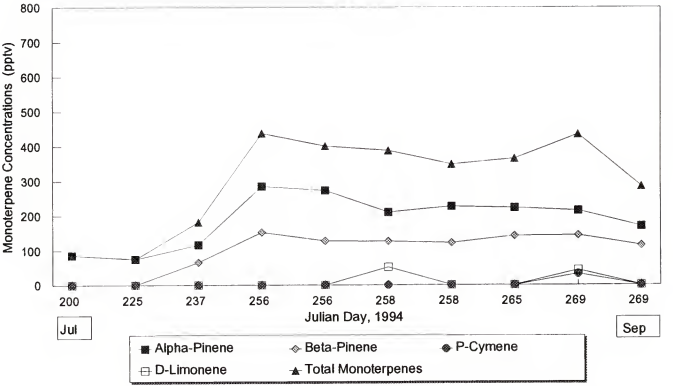


Figure 4-19. Seasonal Ambient Terpene Concentration Trends during the 3rd Quarter of 1994.

values for the July - August period; 114 pptv (RSD = 51 %), as can be seen in Table 4-30. Monthly total monoterpene concentrations were higher in September, 1994 than in July - August and the former values were also more consistent. Overall terpene concentrations in ambient air at Cary Forest for the summer season were from 75 to 438 pptv.

Holdren et al. (1979) reported average ambient terpene levels for July, August, and September 1973 at 100 pptv (60, 60, 180 pptv, RSD = 57% for n=3), 70 pptv (100 and 40 pptv, n=2), and 225 pptv (390 and 60 pptv, n=2), respectively.

Riba et al. (1987) determined that total atmospheric terpene concentrations were less than 500 pptv in the daytime and varied from 2 to 4 ppbv at night at 5 meters above ground in a pine forest in France during September 1985. Roberts et al. (1985) have described monoterpene measurements made during the night at a rural site in the Rocky Mountains. The average night time level of monoterpenes was 630 pptv, but in the day time the average dropped to 270 pptv. Also other investigators have reported that monoterpenes in ambient air occurred at higher concentrations during the night than for daytime conditions (Roberts et al., 1985; Yokouchi et al., 1988). This nighttime increase in ambient monoterpene concentration

Table 4-30. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 3rd Quarter (Summer) of 1994.

	July-August	September	Quarter
Mean	114	380	300
STD	59	54	139
RSD (%)	51	14	46
Minimum	75	285	75
Maximum	181	438	438
Median	86	388	357
N	3	7	10

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

is believed to be mainly due to low levels or absence of reactive chemical species, such as OH and O_3, at night as well as being a result of nighttime atmospheric stability.

Peterson (1988) observed very high ambient monoterpene concentrations in a pine forest in Sweden during nighttime conditions. Air samples were taken just a few centimeters above the ground by an unattended sampler overnight. Total monoterpene levels of the order of 18 ppbv were observed in the summer night air of a typical young planted forest of Scots pine in Sweden.

Isidorov et al. (1985) reported ambient monoterpene concentrations determined in coniferous forests of the U.S.S.R. in the summer season of 1981 and 1982. The most southern and northern points of the collection area were 10 degrees latitude apart. The predominant terpene component present was α-pinene amounting to 40-65% of the total terpenes found. Ambient terpene concentrations measured under the forest canopy generally were in the range from 0.63 ppbv to 6.29 ppbv. Air samples collected over mossy marshes, where terpene concentrations were much higher, were an exception, because myrcene was the major component, rather than α-pinene, which is predominant in the airshed of coniferous forests.

Tropospheric ambient concentrations of methane, C_2-C_{10} hydrocarbons, and CO were measured over the Amazon tropical forest near Manaus, Amazonas, Brazil, in July and August 1985 (Zimmerman et al., 1988). A helium-filled, tethered balloon was used as the sampling platform for the collection of hydrocarbon samples. The measurements were all made within the atmospheric boundary layer up to an altitude of 1000 m above ground level. Ambient monoterpene levels ranged from 60 pptv (at 152 m altitude) to 540 pptv (at 30 m altitude). The samples collected within the forest canopy varied in concentration from 120 to 340 pptv (mean =230 pptv) (Zimmerman et al., 1988).

Fractional ambient concentrations of α-pinene (mean= 0.69) and β-pinene (mean= 0.28) are shown in Figure 4-20 (also see Table 4-31) for the summer season, 1994. Although unusually high terpene levels occurred in August, 1994, fractional HC compositions (FHCs) were similar throughout the season. Relatively low concentrations of p-cymene and d-limonene were observed in September, as shown in Figures 4-19 and 4-20. Beta-pinene FHCs in the 3rd quarter were on the average a little larger than those for the 2nd quarter, 1994.

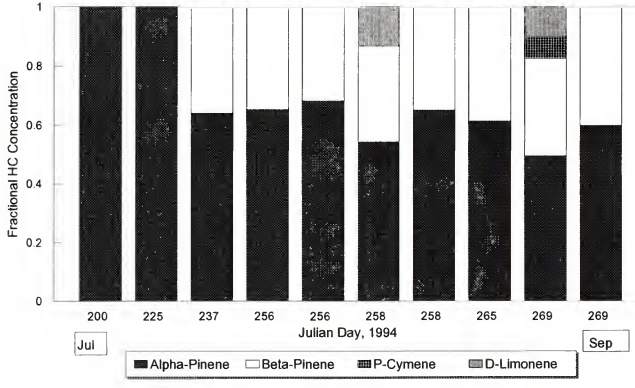


Figure 4-20. Fractional Distributions of Ambient Hydrocarbon Observed during the 3rd Quarter of 1994.

Table 4-31. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 3rd Quarter (Summer) of 1994.

	α-pinene	β-pinene
Mean	0.69	0.28
STD	0.17	0.15
RSD (%)	25	54
Minimum	0.49	< 0.006
Maximum	1	0.4
Median	0.64	0.34
N	10	10

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

Fourth Quarter (Fall) of 1994

Ambient air sample collection during the fall quarter was conducted from October 6, 1994 through December 14, 1994. The terpene levels in October were relatively consistent and provided a mean value of 323 pptv. Two events occurred in November 1994 that resulted in unusually high concentrations (1.53 and 0.69 ppbv) of monoterpenes (Julian days: 306 and 333). It is possible that these unusually high terpene concentrations might have occurred as a result of an atmospheric inversion or unexpected experimental errors.

Ambient temperatures existing at the time, when the high ambient terpene levels were observed, 17.5 °C and 25.5 °C, were relatively low for this time of year. Also, the sky was mostly cloudy in both cases. Holdren et al. (1979), also, have reported unusually high levels of ambient terpenes during the month of November, 1.55 ppbv and 1.40 ppbv. The mean value found in this work for the month of November 1994 was 256 pptv (RSD = 28 %, n = 6), where the two unusually large ambient values were excluded from the estimation. Holdren and co-workers reported a mean concentration of terpenes in ambient air for the same month (November) of 178 pptv (RSD=61.7%, n=8), where the two unusually large values they

observed were excluded from calculation of the mean. The ambient terpene levels found in ambient air at Cary Forest for December 1994 were observed to decrease considerably from the levels found for previous months. These lower levels were probably a result of low temperatures and lower solar radiation intensities occurring late in the year. The mean terpene level estimated for December 1994 was 106 pptv (see Table 4-32). It is possible that ambient terpene levels for October were relatively higher than those for November and December because the daytime average ambient air temperatures were higher in October.

The overall mean concentration of terpenes for the fall quarter was 248 pptv, when the two unusually high concentrations observed in November were excluded. Delta-limonene levels were measurable in November, in addition to α-pinene and β-pinene. Although absolute ambient terpene levels varied considerably during the fall quarter, 1994, as shown in Figure 4-21, the relative abundances were consistent throughout 4th quarter of 1994 (see Figure 4-22). Mean fractional ambient concentrations of α-pinene and β-pinene were 0.53 and 0.46, respectively, during the fall of 1994 (see Table 4-33).

Table 4-32. Statistical Analysis of Ambient Total Terpene Concentrations (pptv) during the 4th Quarter (Fall) of 1994.

	October	November	December	Quarter
Mean	323	256	106	248
STD	82	71	43	176
RSD (%)	25	28	40	71
Minimum	267	163	62	62
Maximum	468	331	148	468
Median	289	264	109	276
N	5	6	3	14

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

Table 4-33. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 4rd Quarter (Fall) of 1994.

	α-pinene	β-pinene
Mean	0.53	0.46
STD	0.04	0.05
RSD (%)	7.8	11
Minimum	0.45	0.35
Maximum	0.6	0.55
Median	0.55	0.45
N	14	14

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

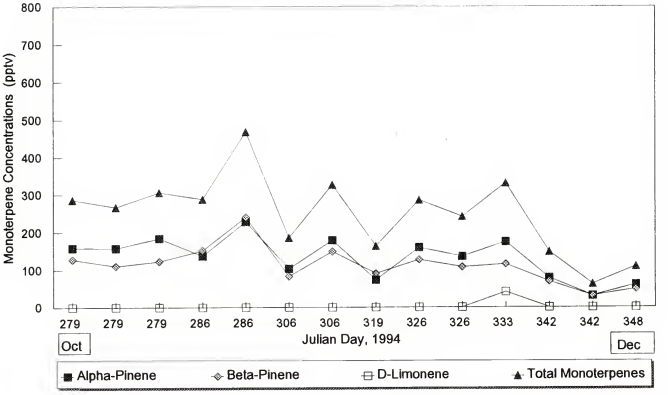


Figure 4-21. Seasonal Ambient Terpene Concentration Trends during the 4th Quarter of 1994.

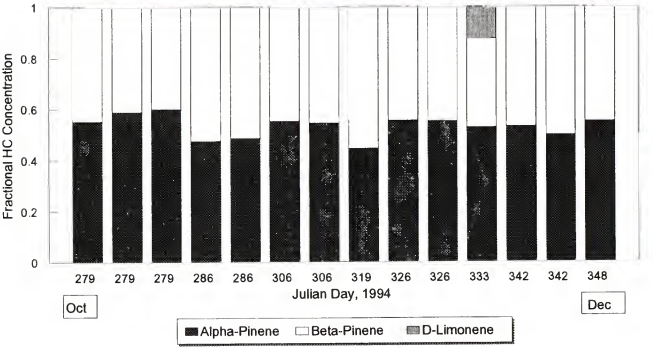


Figure 4-22. Fractional Distributions of Ambient Hydrocarbon Observed during the 4th Quarter of 1994.

First Quarter (Winter) of 1995

During the winter quarter ambient air samples were collected from January 21, 1995 through March 29, 1995. Monoterpene levels observed during this winter season were low in comparison with samples collected during other seasons, as expected (see Figure 4-23). It is likely that these low levels occurred because ambient temperatures were low, in the range from 12.2 to 24.6 °C. In addition, solar radiation intensities were lower.

The mean concentration of ambient monoterpenes in January 1995 was estimated at 44 pptv whereas those for February and March, 1995 were 61 and 98 pptv respectively (Table 4-34). The overall mean terpene concentration was 78 pptv for the winter season, 1995.

An unusual event occurred on February 1, 1995 (JD: 32) (see Figure 4-23). Delta-limonene was found to be the most abundant terpene present in an ambient air sample collected on the day and α-pinene was reduced to being immeasurable on this winter day. Also, for this winter day it was observed that the total and individual ambient terpene levels were the lowest recorded for the full year duration of this field project.

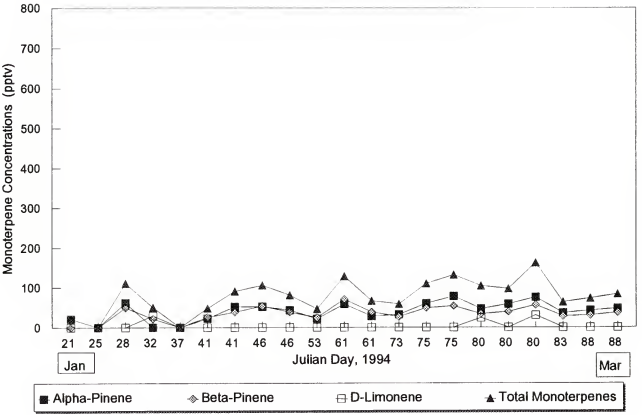


Figure 4-23. Ambient Terpene Concentration Trends during the 1st Quarter of 1995.

Table 4-34. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 1st Quarter (Winter) of 1995.

	January	February	March	Quarter
Mean	44	61	98	78
STD	59	35	33	42
RSD (%)	133	58	34	54
Minimum	< 10	< 10	58	< 10
Maximum	111	106	162	162
Median	22	55	97	81
N	3	7	11	21

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

Table 4-35. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 1st Quarter (Winter) of 1995.

	α-pinene	β-pinene
Mean	0.52	0.43
STD	0.18	0.12
RSD (%)	34	29
Minimum	< 0.02	< 0.02
Maximum	1	0.58
Median	0.54	0.44
N	19	19

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

Quarterly mean fractional hydrocarbon contributions by concentrations by ambient concentrations of α-pinene and β-pinene were 0.52 and 0.45, respectively (see Table 4-35). Although individual concentrations of ambient terpenes were quite variable during the winter quarter, the fractional HC composition were consistent, particularly after the middle of February, 1995, as can be seen in Figure 4-24.

Second Quarter (Spring) of 1995

Ambient air sampling during the spring quarter was conducted from April 3, 1995 through June 14, 1995. Ambient air temperatures during this season were higher during winter season. Also, it was observed that there were more frequent rain events during the spring season in 1995 than for the same period in 1994.

Emission rates of monoterpenes from slash pine trees, the predominant tree specie at the Cary Forest site, were found to be the highest during the spring quarter. Consequently, it was expected that corresponding high ambient levels of terpenes should occur at the Cary Forest site. To the contrary, however, low ambient concentrations of terpenes were observed at the site, as seen in Figure 4-25.

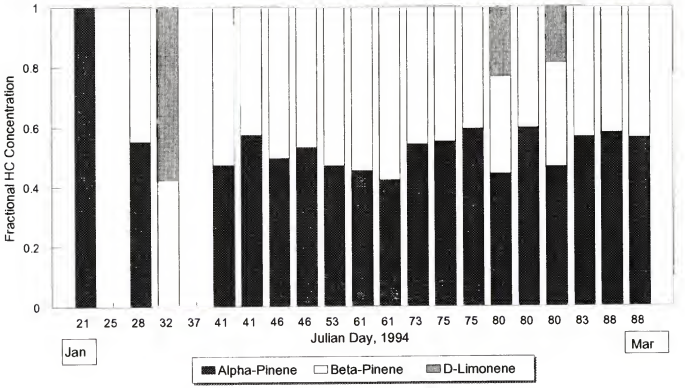


Figure 4-24. Fractional Distributions of Ambient Hydrocarbon Observed during the 1st Quarter of 1995.

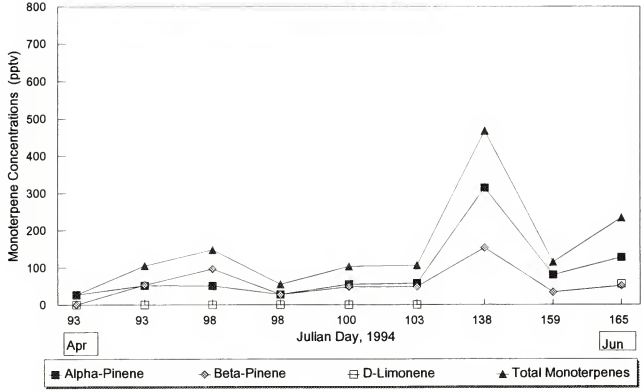


Figure 4-25. Seasonal Ambient Terpene Concentration Trends during the 2nd Quarter of 1995.

The mean ambient concentration obtained for total monoterpenes in April 1995 was 91 pptv whereas that for May and June combined was 271 pptv, as can be seen in Table 4-36. The mean value for April 1995 was 91 pptv whereas in April was much lower than that for the corresponding period in 1994 (256 pptv). Ambient air temperatures increased steadily as the spring season progressed from April to June, 1995. The mean ambient terpene concentration (271 pptv) for the total monoterpenes in May and June of 1995, however, was slightly lower than that for the same period in 1994 (i.e., 331 pptv).

Fractional ambient hydrocarbon values of α-pinene were in the range from 0.34 to 1.0 during the spring of 1995 (see Figure 4-26). Seasonal mean fractional ambient HC compositions for α-pinene and β-pinene were 0.59 and 0.38, respectively (see Table 4-37). It appears, however, that the β-pinene/α-pinene ratio (0.28) for spring of 1994 was much lower than the quarterly average (β/α ratio= 0.64) for the corresponding season, 1995 and the lowest observed during the 15 month field study. Also, it was found that the quarterly average β/α ratios for the fall season 1994 and the winter season 1995 were the highest observed during this project.

Table 4-36. Statistical Analysis of Ambient Terpene Concentrations (pptv) during the 2nd Quarter (Spring) of 1995.

	April	May - June	Quarter
Mean	91	271	151
STD	43	180	132
RSD (%)	47	66	87
Minimum	27	114	27
Maximum	147	467	467
Median	104	233	106
N	6	3	9

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

Table 4-37. Statistical Analysis of the Distribution of Fractional Ambient HC Concentrations during the 2nd Quarter (Spring) of 1995.

	α-pinene	β-pinene
Mean	0.59	0.38
STD	0.18	0.19
RSD (%)	31	51
Minimum	0.34	< 0.02
Maximum	1	0.66
Median	0.54	0.45
N	9	9

Note: STD= Standard Deviation, N= Number of Samples.
RSD (%) = Relative Standard Deviation (%).

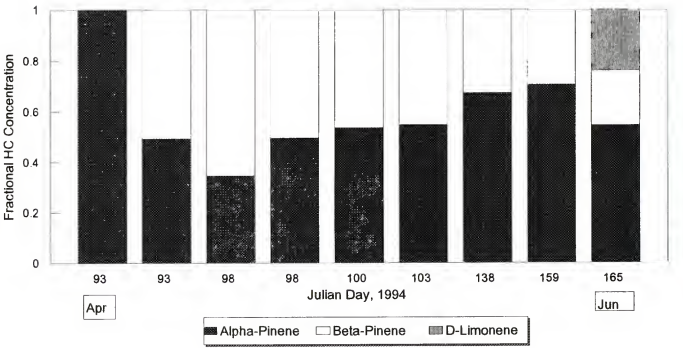


Figure 4-26. Fractional Distributions of Ambient Hydrocarbon Concentration Variations during the 2nd Quarter of 1995.

These results suggested that there might possibly be an influence of local ozone on ambient terpene levels in the spring. Ozone production in spring is greater than in the other seasons (Sutton and Allen, 1990). Some researchers (Winer et al., 1976; Atkinson et al., 1990; Atkinson, 1990) have found that β-pinene has a greater ozone production potential than α-pinene. It would be interesting, therefore, to determine whether a relationship exists between ambient ozone and monoterpene concentrations at the Austin Cary Forest site.

Relationship between Ambient Monoterpene and Ozone Concentrations

It seems reasonable to assess possible correlations between total monoterpene and ozone concentrations on a quarterly basis. Because cloud cover can alternate solar radiation fluxes and ambient air temperatures, chemical reactions and rain can limit terpene emission rates, raindays and cloudy days were excluded from the data analysis. Also, days when unusually high monoterpene levels occurred were excluded from data analysis.

Second Quarter (Spring) of 1994 [4/8/94 - 6/25/94]

During the spring quarter of 1994 the days were very dry (RH = 39.8±9.7%) and it was sunny most of the time. Emission rates of monoterpenes from slash pines were higher than those in summer, 1994. Windy (> 2.5 m/sec) days were observed only twice during this 11 week measurement period.

The highest seasonal daily maximum ozone concentration (92 pptv) in this observation period occurred in May 1994 and hourly average ozone levels frequently exceeded 70 pptv during the quarterly period. Total monoterpene concentrations were found to be negatively correlated with ozone concentrations during the spring season of 1994, as shown in Figure 4-27. The correlation coefficient (r^2 = 0.816, n=14) between the two variables was relatively high for this observation period. A data point (terpene concentration < 2 pptv) was excluded from the regression analysis because it was measured under extreme and inconsistent conditions (windy day, elevated sampling location) as mentioned earlier.

Some ambient air sampling measurements were conducted in the morning hours from 10 a.m. to 12 noon, and others were carried out in the afternoon from 12 noon to 6 p.m. during the spring quarter, 1994. Regression analysis of morning and

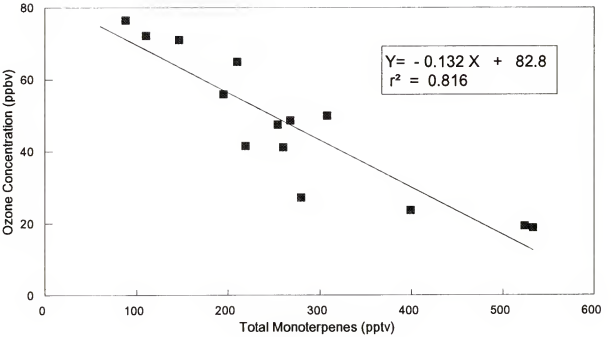


Figure 4-27. Observed Total Monoterpenes Ambient Concentrations versus Ozone Concentrations during the 2nd Quarter, 1994.

afternoon ambient terpene concentrations versus ozone concentrations also correlated reasonably well with correlation coefficient values (r^2) of 0.884 (n = 5) and 0.776 (n = 9), respectively.

Third Quarter (Summer) of 1994 [7/8/94 - 9/26/94]

Rain events during the summer season in north central Florida were more frequent than during the rest of the year. Also, the atmosphere, as a result of summer rains, was more humid at this time than for the other seasons. The in-situ continuous ozone analyzer (Model 46, Thermo Environment, Hopkinton, Mass) was out of service for 7 weeks during the summer months of 1994. As a result ozone data were not available for July and August, 1994.

A high correlation coefficient (r^2 = 0.99, n=3) between the two chemical species was obtained showing that the variables were apparently directly related for a few afternoon samples collected during the summer months. More data is needed, however, to confirm the direct dependence of ambient terpene concentrations on ozone levels because of the minimal data available for the two variables for the summer quarter.

Yokouchi and Ambe (1988) measured ambient monoterpene levels in an agricultural area in Japan during the summer. They observed that the monoterpene concentrations were negatively correlated with ambient ozone concentrations. Although the current study showed a relation inverse to the result obtained from the study in Japan during the summer, this conflicting result might be due to either the different atmospheric conditions existing at the two sampling sites (Japan and U.S.A.) or the lack of data provided by the current study.

Fourth Quarter (Fall) of 1994 [10/6/94 - 12/14/94]

An inverse correlation (r^2 = 0.659, n=7) was found between total monoterpene and ozone concentrations for samples collected during the afternoon hours, from 1 to 6 p.m., during the fall season. Insufficient data were available for the morning hours to warrant correlating the data during the three month fall period study.

Although the ambient temperature range observed during the fall season was similar to that observed during the spring quarter, more cloudy days and precipitation events occurred during the fall quarter of 1994.

First Quarter (Winter) of 1995 [1/21/95 - 3/29/95]

A relatively weak correlation (r^2 = 0.252, n=15) was obtained for the inverse dependence of total monoterpene and ozone concentrations during the winter season. During this period ambient temperatures were relatively low and less intense solar radiation was available during the winter, when compared to the summer months. Trace amounts (below method detection limit) of terpenes were frequently observed in ambient air samples collected during the winter season.

Relationship between Ambient Air Temperatures and Monoterpene Concentrations

Kim et al.(1995) have reported that the emission rate of monoterpenes from slash pine trees at the Austin Cary Forest site appeared to be strongly affected by ambient air temperatures and seasonal changes. As a result, it is to be expected that ambient monoterpene levels should increase as ambient air temperatures increase if there are no significant chemical removal and/or physical dilution processes. Data obtained on days with precipitation events were excluded from this analysis in order to obtain a clear understanding of the dependence of ambient air concentrations of monoterpenes on temperature.

In general, it was found that there are weak correlations for the direct dependence of monoterpene concentrations and ambient air temperatures, as shown in Figure 4-28. Correlation coefficients (r^2) for data obtained during spring (1994), fall (1994), and winter (1995) quarters were 0.622 (n=15), 0.512 (n=14), and 0.315 (n=21), respectively.

An unexpected dependence was found between the ambient air temperature and fractional ambient monoterpene compositions, for samples obtained during the summer (3rd quarter) of 1994. An inverse dependence between the variables was weakly correlated (r^2 = 0.632, n=10). However, Yokouchi and Ambe (1988) reported that the monoterpene concentrations were positively correlated with ambient temperature in Japan during the summer.

The Relationship between Emission Sources and Sinks

The Austin Cary Forest site is surrounded by slash pine trees (> 90 %) and some other tree species (< 10 %). Therefore, if slash pine is the major source of monoterpenes observed in the local ambient air, the fractional hydrocarbon

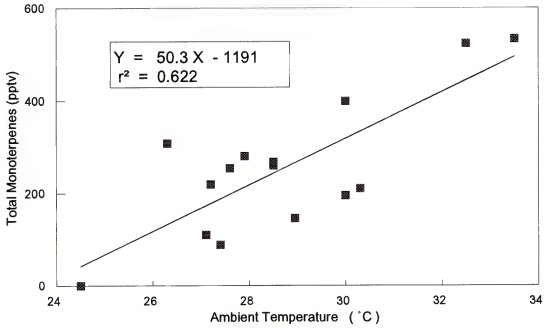


Figure 4-28. Influence of Temperature on Ambient Monoterpene Levels during the 2nd Quarter, 1994.

compositions (or β/α ratios) from both slash pine emission samples and ambient air samples should agree with each other. In general, α- and β-pinenes comprise more than 90 % of the total monoterpenes found in both slash pine emissions and ambient air samples.

During the summer and fall of 1994, there was good agreement between the slash pine emissions and ambient HC compositions (and β/α ratios), as can be seen in Tables 4-38 and 4-39. However, there was a lack of agreement between the two variables during the winter and spring seasons of 1995.

The β/α ratios during the spring of 1994 and 1995 were 0.28 and 0.64, respectively. The reason for the difference might be due to two quite different types of weather conditions existing for the same period in the two consecutive years. The spring of 1994 was drier and received more solar radiation than the corresponding period of 1995. There were less rain events in 1994, as discussed earlier. It is possible that more β-pinene than α-pinene was consumed under the sunny and dry conditions existing in the spring of 1994 at the Cary Forest site.

Table 4-38. The Relationship between the Fractional Hydrocarbon Emission Rates for Slash Pine and Fractional Ambient Hydrocarbon Composition.

Season	Slash Pine	Ambient Air	Slash Pine	Ambient Air
	α-pinene	α-pinene	β-pinene	β-pinene
Spring (94)	N/A	0.78	N/A	0.22
Summer (94)	0.66	0.69	0.27	0.28
Fall (94)	0.48	0.53	0.4	0.46
Winter (95)	0.61	0.52	0.32	0.43
Spring (95)	0.67	0.59	0.25	0.38

note: N/A = not available.

Table 4-39. Comparison of β/α Ratios for Slash Pine Emission and Ambient Air Samples.

Season	Slash Pine	Ambient Air
Spring (94)	N/A	0.28
Summer (94)	0.41	0.41
Fall (94)	0.83	0.87
Winter (95)	0.52	0.83
Spring (95)	0.37	0.64

note: N/A = not available.

Based on the data in Tables 4-38 and 4-39 it appears that the monoterpenes present in the ambient air were primarily emitted from slash pines surrounding the Cary Forest site.

Atkinson (1990) summarized the chemical reactivities between several monoterpenes and O_3 and between monoterpenes and OH radical. He reported that the relative reactivity of α-pinene with O_3 is 5.3 times higher than that of β-pinene, while that of d-limonene is 40 times higher. It was also reported that β-pinene and d-limonene have 1.2 and 2.6 times more potential to produce O_3 than α-pinene, respectively.

If the β/α ratios of pine tree emissions in 1994 were similar to those in 1995, it could be possible that the spring time ambient β/α ratio (0.28) in 1994 had more potential to have produced ozone than the ratio (β/α = 0.64) in 1995 (see Table 4-38). On the contrary, the winter for 1995 (β/α = 0.83) and the spring for 1995 (β/α = 0.64) could have had more potential to titrate ozone than to produce ozone because the β/α ratios were relatively higher than expected (see Table 4-38).

During the whole sampling period the ambient concentrations of myrcene, d-limonene, β-phellandrene were

negligible most of the time. The reason for these low concentrations might be due to these terpenes having at least two double bonds and being more reactive than α-pinene or β-pinene in the ambient air (Winer et al., 1976).

Effects of Age on Slash and Loblolly Pine Emissions

Field sampling was conducted only during day time hours on 3 to 4 years old saplings at the Cary Forest site. The majority of pine trees surrounding Cary Forest air quality monitoring site were 19 year old mature slash pine trees.

Fractional hydrocarbon compositions and β/α ratios for slash pine trees between 4 and 7 years were compared for a short duration as shown in Table 4-40. No substantial differences were found in the fractional values for the two different age groups of pine trees; however, the TERs from the older trees were approximately 10 times lower than those for the younger trees. This difference suggested that although the ages of trees might not affect the fractional HC compositions they could affect the total terpene emission rates, as discussed earlier (Johnson and Allen, 1994).

Table 4-40. Comparison of the Fractional Hydrocarbon Compositions and the β/α Ratios between 4 and 7 year old Slash Pine Trees.

Sampling Dates & Mature Stages of Trees	Monoterpene Compositions and β/α Ratios			
	Temperature (°C)	**α-Pinene**	**β-Pinene**	**β/α Ratios**
Mar 29, 1995				
4 years old Tree	26.9	0.72	0.22	0.31
7 years old Tree	22.6	0.71	0.29	0.41
Apr 10, 1995				
4 years old Tree	30.4	0.64	0.27	0.41
7 years old Tree	30.5	0.52	0.3	0.58
<<Average>>				
4 years old Tree	28.7	**0.68**	**0.24**	**0.36**
7 years old Tree	26.6	**0.61**	**0.3**	**0.5**

Long Term Variations in Pine Tree Emission Rates and Ambient Terpene Concentrations

Total monoterpene emission rates measured between July, 1994 and June, 1995 from slash and loblolly pine trees were averaged over monthly periods to develop an understanding of seasonal and annual trends (see Table 4-41). Quarterly seasonal averages of total terpene emission rates from both pine species are shown in Table 4-42.

Slash pine tree total TERs shown in Figure 4-29 and summarized in Table 4-42 revealed that the highest emissions occurred in spring and summer seasons and lowest emissions in fall and winter seasons.

Loblolly pine tree total TERs shown in Figure 4-30 and summarized in Table 4-42 indicated that the emission rates were highest in summer and were consistently low at for the rest of the year.

Ambient levels of total terpenes for the period from April 1994 through June 1995, shown in Figure 4-31, showed some evidence of annual trends similar to those for slash pine emission rates.

Table 4-41. Monthly and Annual Averages of Total Terpene Emission Rates (TERs) ($\mu g/m^2$-hr) from Slash and Loblolly Pine Trees.

Month (Year)	Slash Pine Total TERs	Loblolly Pine Total TERs
Jul (1994)	240 (2)	239 (2)[1]
Aug	260 (2)	75 (2)
Sep	197 (3)	14 (5)
Oct	135 (3)	8.1 (1)
Nov	57.9 (2)	9.4 (1)
Dec	46.9 (1)	N/A
Jan (1995)	4.8 (1)	25 (3)
Feb	44 (8)	16 (4)
Mar	272 (4)	8.8 (2)
Apr	157 (3)	11.9 (2)
May	253 (2)	31.2 (2)
Jun	278 (2)	11.7 (2)
Annual Average	**162 (33)**	**40.9 (26)**
Std. Dev.	102	68
Rel. std. dev. (%)	63	167
Minimum	4.8	8.1
Maximum	278	239
Median	177	14
Number of Months	12	11

Note: N/A = not available. Anomalous data (e.g., for rain events) excluded. Number (n) of samples used to estimate averages shown in parentheses. Limitations: Daytime measurements only from saplings from July, 1994 to June, 1995.

[1]One from end of June and one from July.

Table 4-42. Quarterly Average of Total Monoterpene Emission Rates (TERs) ($\mu g/m^2$-hr) from Slash and Loblolly Pine Trees.

Quarter (Year)	Slash Total TERs	Loblolly Total TERs
3rd Quarter (94)	232 (7)	109 (9)
4th Quarter (94)	79.9 (6)	8.8 (2)
1st Quarter (95)	106 (13)	16.6 (9)
2nd Quarter (95)	229 (7)	18.3 (6)
Annual Average	**162 (33)**	**40.9 (26)**

Note: N/A = not available. Anomalous data (e.g., for rain events) excluded. Number (n) of samples used to estimate averages shown in parentheses.
Limitations: Daytime measurements only from saplings from July, 1994 to June, 1995.
Temperature range: 9.8 - 34.5 °C.

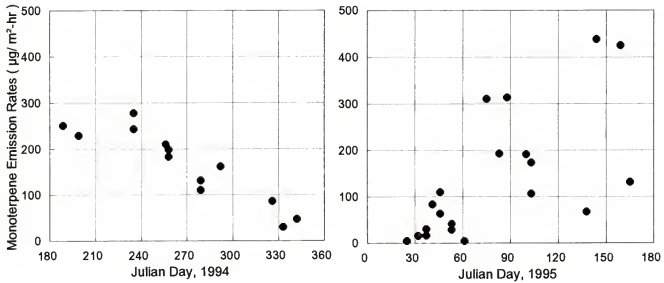


Figure 4-29. Variation of Total Monoterpene Emission Rates from Slash Pine Saplings from July 8, 1994 to June 14, 1995.

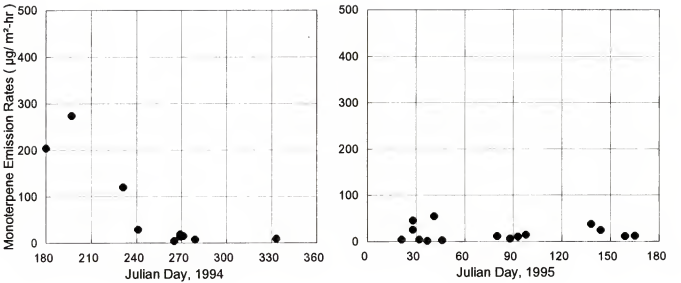


Figure 4-30. Variation of Total Monoterpene Emission Rates from Loblolly Pine Saplings from June 27, 1994 to June 14, 1995.

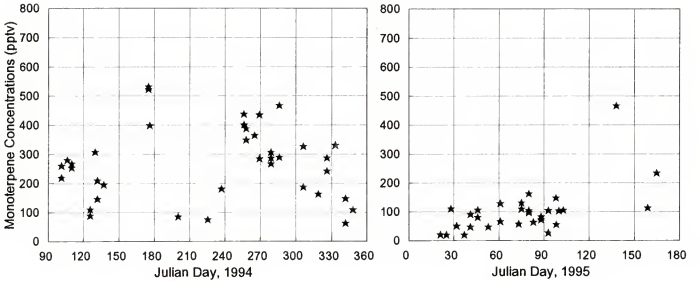


Figure 4-31. Variation of Total Monoterpene Concentrations in Ambient Air from April 11, 1994 to June 14, 1995.

CHAPTER 5
CONCLUSIONS

Development of Analytical and Sampling Approaches

In this research, a method involving an automated desorbing and cryogenic focusing system coupled to a GC was, developed, tested and used for monoterpene measurements.

The use of carefully prepared individual monoterpene hydrocarbons dissolved in methanol and stored in sealed glass vials in a cool and dark environment proved to have long term (< 5 % change in 12 months) stability. These standard solutions (liquid phase standards) could then be used for direct injection to a sorbent tube or to a flowing inert gas (gas phase standards) for subsequent transfer and analysis. Standard recoveries (accuracy) were typically greater than 95% and replicate variations (reproducibility) were less than 1%.

A more reliable, practical, and cost effective tree emission sampling method was developed and tested. The modified vegetation enclosure technique (VET) showed good

precision (RSD< 15%) at similar temperature conditions (± 1°C) and good recovery (>90%) from a series of tests.

Emission Rate Measurements

Although variations in the fractional hydrocarbon composition of emission samples (FHER) for slash pines were observed, the average terpene composition was fairly consistent throughout the year. It was found that α-pinene (61%, highest in spring and summer) and β-pinene (31%, highest in fall) were the most abundant compounds emitted from slash pines regardless of season. Delta-limonene, β-phellandrene, and myrcene always comprised less than 10% of total monoterpene emissions.

Fractional HC emissions (FHER) from loblolly pines showed marked seasonal variations when compared to slash pine emissions. Loblolly pine TER variations during the summer and fall were large. Alpha-pinene was found to be the most abundant monoterpene emitted from loblolly (62%, highest in winter) and slash pines (61%), regardless of season. Beta-pinene emitted from loblolly pines was not a significant contributor (6%) to total monoterpene emissions as that from

slash pine. Myrcene (13%), d-limonene and β-phellandrene (20%) emissions from loblolly pine were relatively high during the summer and fall seasons. Only trace amounts of camphene were found in emissions from both slash and loblolly pines.

Seasonal maximum TERs occurred during the spring and summer seasons for slash pines. Terpene emission rates during the summer (July - August) were as high as those observed in spring. The TERs decreased in September and continued to decrease throughout the fall season as average air temperatures decreased.

Loblolly pine emissions for a similar temperature range revealed different seasonal patterns of emissions compared to those for slash pine. The highest emissions of loblolly pine occurred in summer (maximum in July) and the emissions slowly decreased in August but dropped drastically after September of 1994 and remained constant until the spring of 1995. The lowest terpene emission rates from both slash and loblolly pines were obtained during the winter months.

It was found that slash pine emissions were more sensitive to environmental temperature conditions than loblolly pine emissions, regardless of seasonal physiological variables. Loblolly pine emissions were not as sensitive as

to temperature changes until early in the summer season. Apparently, seasonal development factors are more important for loblolly than for slash pine emissions.

It was determined that temperature, seasonal change (e.g. bud emission), ages of trees (Johnson and Allen ,1994), surface wetness (rain event), and natural rough handling (e.g., strong wind, insect attack) were factors affecting TERs from both slash and loblolly pines. Johnson and Allen (1994) found that soil fertility is also a significant factor controlling terpene emission rates from slash and loblolly pines.

Loblolly pine trees were more sensitive to rough handling (e.g., touching, grabbing) than slash pines.

Ambient Air Measurements

Monoterpene compounds that were characterized in ambient air samples from the Cary Forest site included; α-pinene, β-pinene, d-limonene, β-phellandrene, and p-cymene, where the latter two compounds were usually below method detection limits (~ 2 pptv based on a 20 L air sample). Alpha-pinene

(61%) and β-pinene (37%) were found to be the most abundant monoterpenes in the forest air.

It was observed that ambient monoterpene levels during winter time were lowest. It is reasonable to believe that the lowest ambient concentration occurred in winter because pine emission rates during winter were lowest.

It was found that ambient terpene concentrations fluctuated frequently during summer. After September the ambient terpene levels decreased as average ambient temperatures decreased slowly following similar declines in TER from slash pine.

Fractional hydrocarbon composition in emissions from slash pine and fractional ambient hydrocarbon compositions were similar during the summer and fall seasons. This observation suggests that slash pine emissions are the principal source controlling ambient terpene levels at the Austin Cary Forest site. However, there was disagreement between the two fractional composition variables during the winter and spring of 1995. The latter disagreement was possibly due to intervention of environmental conditions which may have affected chemical reactions of atmospheric monoterpenes.

It was found that total monoterpene concentrations were negatively correlated with ozone during the spring, fall, and winter seasons. However, a positive correlation between terpene and ozone was observed only for summer afternoons.

It was observed that there were positive correlations between the ambient temperature and monoterpene concentrations during the spring, fall, and winter except summer.

CHAPTER 6
RECOMMENDATIONS

More studies are needed to measure emissions from buds on pine trees. New studies are justified due to the high emission rates observed during bud development.

Trace levels of isoprene were observed from slash pines in the spring and summer. Isoprene may originate from developing pine buds during spring when the buds accumulate significant amounts of resins. However, because isoprene is a very reactive compound it may quickly react with other oxygenated compounds as soon as it is emitted from pine needles. It is, therefore, recommended that a mixture of nitrogen and carbon dioxide be used instead of zero air to maximize isoprene collection when sampling emissions during sunny days.

Previous researchers have shown that soil fertility could affect terpene emission rates (TERs) from slash and loblolly pines. To study this effect it is necessary to observe the

influences of soil type and tree density (tree spacing) on TERs from pine trees.

More studies of the effects of needle or leaf surface wetness on pine emissions are needed during different seasons in order to develop a better understanding of the mechanisms involved.

Simultaneous TER sampling from different heights or locations on the same pine trees are necessary in order to validate a representative sampling methodology through an investigation of the differences in NMHC samples under a variety of conditions.

Wind and insect effects on slash and loblolly pine emissions are not clear. More seasonal wind and insect effect studies are needed to understand this complex and influential TER factor.

One of the disadvantages using a sorbent tube (e.g., Tenax tube) sampling approach is the sampling flow-rate limit. A multiple tube sampler and desorber system may solve this problem, i.e., a higher flow rate can be handled using multiple tubes mounted in parallel.

Seasonal change effects on diurnal cycle measurements of ambient terpene levels and terpene emission rates are required

to better understand local and short-term environmental factors.

A design for a larger enclosure bag (> 40 L) is needed to enclose longer needles and minimize rough handling effect.

The current and previous studies at the Cary Forest site suggest that the site can be treated as a simple chemical reactor. Continuous monitoring of meteorological and air quality variables are needed to observe NO/NO_2, O_3, HCs and to investigate their relationship to ambient levels and emission rates of terpene hydrocarbons.

Springtime ozone levels were higher than in summer. Ozone and water vapor pressure showed a good direct correlation during spring. However, the role of water vapor in ozone production during spring and summer needs to be better understood.

Rain simulation (surface wetness effect) and pine tree age effects suggest an overestimation of monoterpene emissions is possible if emission data from seedlings or saplings are used for inputs to ozone models.

Ozone simulation models require an accurate biogenic emission inventory. The importance of these biogenic hydrocarbons may be possibly underestimated in terms of ozone

production potential due to lack of accurate biogenic emission inventories. More extensive studies are needed to provide reliable estimates of biogenic hydrocarbon emission rates from different types and ages of trees in different locations and for different weather conditions.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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